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Office of Naval Research

End-of-Year Report

Publications/Patents/Presentations/Honors/Students Reports

for

Contract N00014-89-J-1893
R&T Code 4132055

Copolymers for Drag Reduction in Marine Propulsion:

New Molecular Structures with Enhanced Effectiveness

PRINCIPAL INVESTIGATORS

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Department of Polymer Science
The University of Southern Mississippi
Hattiesburg, Mississippi 39406-0076

May 31, 1992

PART I

Office of Naval Research
Publications/Patents/Presentations/Honors Report

R&T Number:	4132055
Contract/Grant Number:	N00014-89-J-1893
Contract/Grant Title:	Copolymers for Drag Reduction in Marine Propulsion: New Molecular Structures with Enhanced Effectiveness
Principal Investigators:	Charles L. McCormick and Roger D. Hester
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a. Number of papers submitted to refereed journals, but not published: 7
b. Number of papers published in refereed journals (list attached): 7
c. Number of books or chapters submitted, but not yet published: 0
d. Number of books or chapters published (list attached): 9
e. Number of preprints: 5
f. Number of patents filed: 0
g. Number of patents granted (list attached): 0
h. Number of invited presentations at workshops or professional society meetings: 1
i. Number of presentations at workshops or professional society meetings: 26
j. Honors/awards/prizes for contract/grant employees (list attached): 1
k. Total number of graduate students and post-doctoral associates supported by at least 25% during this period, under this R&T project number:
   Graduate Students: 11
   Post-Doctoral Associates: 1
   including the number of,
   Female Graduate Students: 1
   Minority Graduate Students: 1
   Asian Graduate Students: 2
l. Other funding (list attached)

A. Papers Submitted to Refereed Journals

"Water-Soluble Copolymers. 26. Fluorescence Probe Studies of Hydrophobically-Modified Maleic Acid-Ethyl Vinyl Ether Copolymers," C. L. McCormick, C. E. Hoyle and M. D. Clark, accepted by *Polymer*.

"Water-Soluble Copolymers. 38. Synthesis and Characterization of Terpolymers of Acrylamide, N-(4-Butyl)Phenylacrylamide and Sodium Acrylate, Sodium-2-Acrylamido-2-Methylpropanesulfonate or Sodium-3-Acrylamido-3-Methylbutanoate," C. L. McCormick, J. C. Middleton, and C. E. Grady, in press, *Polymer*.

"Water Soluble Copolymers. 42. Cationic Polyelectrolytes of Acrylamide and 2-Acrylamido-2-Methylpropanetrimethylammonium Chloride," C. L. McCormick and L. C. Salazar, accepted by *J. Polymer Science, Part A—Polymer Chem.*

"Water Soluble Copolymers. 44. Ampholytic Terpolymers of Acrylamide with Sodium 2-Acrylamido-2-Methylpropanesulfonate and 2-Acrylamido-2-Methylpropanetrimethylammonium Chloride," C. L. McCormick and L. C. Salazar, accepted by *Polymer*.

"Water Soluble Copolymers. 45. Apholytic Terpolymers of Acrylamide with Sodium 3-Acrylamido-3-Methylbutanoate and 2-acrylamido-2-Methylpropanetrimethylammonium Chloride," C. L. McCormick and L. C. Salazar, accepted by *J. Applied Polymer Sci.*

"Water Soluble Copolymers 46. Hydrophilic Sulfobetaine Copolymers of Acrylamide and 3-(2-Acrylamido-2-Methylpropanedimethylammodio)-1-Propanesulfonate," C. L. McCormick and L. C. Salazar, accepted by *Polymer*.

"A High Reynolds Number Rotating Disk Rheometer," J. P. Dickerson, L. M. Flesher and R. D. Hester, submitted to *J. Physics E: Scientific Instruments*, March 1992.

B. Papers Published in Refereed Journals

"Size-Exclusion Chromatography of High Molecular Weight Water-Soluble Polymers," A. M. Saffieddine and R. D. Hester, *J. Applied Polymer Sci.* **1991**, *43*, 1987-1990.

"Water-Soluble Copolymers. 37. Synthesis and Characterization of Responsive Hydrophobically Modified Polyelectrolytes," C. L. McCormick, J. C. Middleton, and D. F. Cummins, *Macromolecules* **1992**, *25(4)*, 1201-1206.

"Apparent Solubility Parameters from Photophysical Investigation of Copolymers with Pendent Naphthyl Chromophores," C. L. McCormick, C. E. Hoyle, M. D. Clark, and T. A. Schott, *Polymer International* **1992**, *27(1)*, 63-65.

"Water-Soluble Copolymers. 39. Synthesis and Solution Properties of Associative Acrylamido Copolymers with Pyrenesulfonamide Fluorescence Labels," C. L. McCormick and S. A. Ezzell, *Macromolecules* **1992**, *25(7)*, 1881-1886.

"Water-Soluble Copolymers. 40. Photophysical Studies of the Solution Behavior of Associative Pyrenesulfonamide-Labelled Polyacrylamides," C. L. McCormick, C. E. Hoyle, D. Creed and S. A. Ezzell, *Macromolecules* **1992**, *25(7)*, 1887-1895.

"Water Soluble Copolymers. 41. Copolymers of Acrylamide and Sodium 3-Acrylamido-3-Methylbutanoate," C. L. McCormick and L. C. Salazar, *J. Macromol. Sci.—Pure Appl. Chem.* **1992**, *A29(3)*, 193-205.

"Water Soluble Copolymers. 43. Ampholytic Copolymers of Sodium 2-Acrylamido-2-Methylpropanesulfonate with 2-Acrylamido-2-Methylpropanetrimethylammonium Chloride," C. L. McCormick and L. C. Salazar, *Macromolecules* **1992**, *25(7)*, 1896-1900.

D. Books or Chapters Published

Water-Soluble Polymers: Synthesis, Solution Properties, and Applications, S. W. Shalaby, C. L. McCormick and G. B. Butler, Eds.; ACS Symposium Series 467; American Chemical Society: Washington, DC, 1991.

"Synthesis and Solution Behavior of Electrolyte-Responsive Polyampholytes," L. C. Salazar, Ph.D. Dissertation, The University of Southern Mississippi, August 1991.

"Structural Design of Water-Soluble Copolymers," C. L. McCormick, *Water-Soluble Polymers: Synthesis, Solution Properties, and Applications*, ACS Symposium Series 467, 1991, Chapter 1, pg. 2.

"Copolymers of Acrylamide and a Novel Sulfobetaine Amphoteric Monomer," L. C. Salazar and C. L. McCormick, *Water-Soluble Polymers: Synthesis, Solution Properties, and Applications*, ACS Symposium Series 467, 1991, Chapter 7, pg. 119.

"Synthesis and Solution Characterization of Pyrene-Labeled Polyacrylamides," S. A. Ezzell and C. L. McCormick, *Water Soluble Polymers: Synthesis, Solution Properties, and Applications*, ACS Symposium Series 467, 1991, Chapter 8, pg. 130.

"Determination of Molecular-Weight Distribution of Water-Soluble Macromolecules by Dynamic Light Scattering," M. J. Mettille and R. D. Hester, *Water Soluble Polymers: Synthesis, Solution Properties, and Applications*, ACS Synposium Series 467, 1991, Chapter 18, 276.

"Photophysical and Rheological Studies of the Aqueous-Solution Properties of Naphthalene-Pendent Acrylic Copolymers," M. D. Clark, C. L. McCormick and C. E.

Hoyle, *Water Soluble Polymers: Synthesis, Solution Properties, and Applications,* ACS Symposium Series 467, 1991, Chapter 19, pg. 291.

"Roles of Molecular Structure and Solvation on Drag Reduction in Aqueous Solutions," C. L. McCormick, S. E. Morgan and R. D. Hester, *Water Soluble Polymers: Synthesis, Solution Properties, and Applications,* ACS Symposium Series 467, 1991, Chapter 21, pg. 320.

"Rheological Properties of Hydrophobically Modified Acrylamide-Based Polyelectrolytes," J. C. Middleton, D. F. Cummins and C. L. McCormick, *Water Soluble Polymers: Synthesis, Solution Properties, and Applications,* ACS Symposium Series 467, 1991, Chapter 22, pg. 338.

E. Preprints

"Hydrophobically Associating Water Soluble Copolymers for the Study of Drag Reduction," P. S. Mumick and C. L. McCormick, *ANTEC Conference Proceedings* **1992**, *38*, 2095-2099.

"Proposed Mechanism for Drag Reduction in Dilute Polymer Solutions," J. P. Dickerson and R. D. Hester, submitted April 1992 for presentation at the National ACS Meeting, Washington, DC, August 1992.

"^{23}Na NMR Studies of Ion-Binding to Anionic Polyelectrolytes," J. K. Newman and C. L. McCormick, submitted April 1992 for presentation at the National ACS Meeting, Washington, DC, August 1992.

"Synthesis and Solution Characterization of Cationic, Hydrophobically-Modified Acrylamide Copolymers," Y. Chang and C. L. McCormick, submitted April 1992 for presentation at the National ACS Meeting, Washington, DC, August 1992.

"Water Soluble Polyampholytes for the Study of Drag Reduction," P. S. Mumick, P. M. Welch and C. L. McCormick, submitted April 1992 for presentation at the National ACS Meeting, Washington, DC, August 1992.

H. Invited Presentations at Workshops or Professional Society Meetings

"Microheterogeneous Associations in Aqueous Solutions," C. L. McCormick, Frontiers in Polymer Science Gordon Research Conference on Ion-Containing Polymers, New London, NH, August 1991.

"Effect of Polymer Microstructure on Drag Reduction Efficiency in Aqueous Media," C. L. McCormick, R. D. Hester and P. S. Mumick, U.K. Makro Group Meeting, University of Durham, Durham, U.K., April 1992.

"Studies of Microheterogeneous Associations in Aqueous Solutions Utilizing Synthetically Tailored Copolymers with Fluorescent Labels," C. L. McCormick, S. A. Ezzell, M. C. Kramer, and K. D. Branham, U.K. Makro Group Meeting, University of Durham, Durham, U.K., April 1992.

I. Presentations at Workshops or Professional Society Meetings

"Effect of Polymer Microstructure and Hydration on Drag Reduction," P. S. Mumick, P. M. Welch and C. L. McCormick, Marine Technology Society Annual Conference, New Orleans, LA, November 11-13, 1991.

"Study of Polymeric Drag Reduction By a Rotating Disk Rheometer," L. M. Flesher and R. D. Hester, Marine Technology Society Annual Conference, New Orleans, LA, November 11-13, 1991.

"Accoustical Analysis of Drag Reducing Polymer Systems," J. P. Dickerson and R. D. Hester, Marine Technology Society Annual Conference, New Orleans, LA, November 11-13, 1991.

"Synthetically Modified Chitin Biopolymers with Potential Commercial Utility," S. Williamson, S. Wolfe, M. Kramer, and C. L. McCormick, Marine Technology Society Annual Conference, New Orleans, LA, November 11-13, 1991.

"Electrolyte-Tolerant, Water-Soluble Copolymers for Off-Shore Enhanced Oil Recovery," K. Branham, E. Kathmann, M. Kramer, and C. L. McCormick, Marine Technology Society Annual Conference, New Orleans, LA, November 11-13, 1991.

"Recombinant Synthesis of Hydrophobically Associating *De Novo* Proteins: Possible Applications for Marine Spill Clean-Up," M. J. Logan and C. L. McCormick, Marine Technology Society Annual Conference, New Orleans, LA, November 11-13, 1991.

"Dilute Solution and Drag Reduction Properties of Polyampholytes," P. M. Welch, P. S. Mumick and C. L. McCormick, 1992 Annual Meeting of the Mississippi Academy of Sciences, Biloxi, MS, March 13, 1992.

"Recombinant Synthesis of Hydrophobically Associating *De Novo* Polypeptides," M. J. Logan and C. L. McCormick, 1992 Annual Meeting of the Mississippi Academy of Sciences, Biloxi, MS, March 13, 1992.

"Synthesis and Characterization of Hydrophobically-Modified Acrylamide/Acrylic Acid Terpolymers," D. L. Davis, K. D. Branham and C. L. McCormick, 1992 Annual Meeting of the Mississippi Academy of Sciences, Biloxi, MS, March 13, 1992.

"Solution Properties of Acrylamide/Acrylic Acid-Based Model Associative Thickeners," K. D. Branham, D. L. Davis and C. L. McCormick, 1992 Annual Meeting of the Mississippi Academy of Sciences, Biloxi, MS, March 13, 1992.

"Rheological and Photophysical Characterization of Poly(Acrylamide-Co-Sodium 11-Acrylamidoundecanoate)," C. G. Farmer, M. C. Kramer and C. L. McCormick, 1992 Annual Meeting of the Mississippi Academy of Sciences, Biloxi, MS, March 13, 1992.

"Synthesis and Characterization of Copolymers of N-Vinyl Formamide and Sodium Acrylate," E. Kathmann and C. L. McCormick, 1992 Annual Meeting of the Mississippi Academy of Sciences, Biloxi, MS, March 13, 1992.

"Synthesis and Solution Characterization of Hydrophobically-Modified Acrylamide Copolymers," Y. Chang and C. L. McCormick, 1992 Annual Meeting of the Mississippi Academy of Sciences, Biloxi, MS, March 13, 1992.

"^{23}Na NMR Studies of Conformational Changes in Hydrophobically-Modified Polymethacrylic Acid Copolymers," J. K. Newman and C. L. McCormick, 1992 Annual Meeting of the Mississippi Academy of Sciences, Biloxi, MS, March 13, 1992.

"Synthesis and Characterization of Pyrene-Labelled Poly (Sodium 11-Acrylamido-undecanoate)," M. C. Kramer, C. G. Farmer and C. L. McCormick, 1992 Annual Meeting of the Mississippi Academy of Sciences, Biloxi, MS, March 13, 1992.

"Rheological and Photophysical Investigation of Water-Soluble Polymers Based on Sodium 11-Acrylamidoundecanoate," M. C. Kramer, C. G. Farmer and C. L. McCormick, Fourth Annual Southeastern Graduate Polymer Conference, Baton Rouge, LA, March 22-25, 1992.

"Solution Properties of Hydrophobically-Modified Polyelectrolytes," K. D. Branham, D. L. Davis and C. L. McCormick, Fourth Annual Southeastern Graduate Polymer Conference, Baton Rouge, LA, March 22-25, 1992.

"Effect of Intramolecular Hydrophobic Associations and Hydration on Drag Reduction," P. S. Mumick and C. L. McCormick, Fourth Annual Southeastern Graduate Polymer Conference, Baton Rouge, LA, March 22-25, 1992.

"^{23}Na NMR Studies of Ion-Binding to Anionic Polyelectrolytes," J. K. Newman and C. L. McCormick, Fourth Annual Southeastern Graduate Polymer Conference, Baton Rouge, LA, March 22-25, 1992.

"Effect of Polymer Microstructure on Drag Reduction Efficiency in Aqueous Media," C. L. McCormick, R. D. Hester and P. S. Mumick, U.K. Makro Group Meeting, University of Durham, Durham, U.K., April 1992.

"Studies of Microheterogeneous Associations in Aqueous Solutions Utilizing Synthetically Tailored Copolymers with Fluorescent Labels," C. L. McCormick, S. A. Ezzell, M. C. Kramer, and K. D. Branham, U.K. Makro Group Meeting, University of Durham, Durham, U.K., April 1992.

"Hydrophobically Associating Water Soluble Copolymers for the Study of Drag Reduction," P. S. Mumick and C. L. McCormick, SPE Annual Technical Conference, Detroit, MI, May 1992.

"Proposed Mechanism for Drag Reduction in Dilute Polymer Solutions," J. P. Dickerson and R. D. Hester, submitted April 1992 for presentation at the National ACS Meeting, Washington, DC, August 1992.

"^{23}Na NMR Studies of Ion-Binding to Anionic Polyelectrolytes," J. K. Newman and C. L. McCormick, submitted April 1992 for presentation at the National ACS Meeting, Washington, DC, August 1992.

"Synthesis and Solution Characterization of Cationic, Hydrophobically-Modified Acrylamide Copolymers," Y. Chang and C. L. McCormick, submitted April 1992 for presentation at the National ACS Meeting, Washington, DC, August 1992.

"Water Soluble Polyampholytes for the Study of Drag Reduction," P. S. Mumick, P. M. Welch, R. D. Hester and C. L. McCormick, submitted April 1992 for presentation at the National ACS Meeting, Washington, DC, August 1992.

J. Honors/Awards/Prizes for Contract/Grant Employees

Invited lecture, Frontiers in Polymer Science Gordon Research Conference on Ion-Containing Polymers, "Microheterogeneous Associations in Aqueous Solutions," C. L. McCormick, New London, NH, August 1991.

K. Graduate Students/Undergraduate Students/Post-Doctoral Associates

Graduate Students:

Dr. Luis C. Salazar—graduated August 1991, joined Texaco Research and Development, Port Arthur, TX
Chase J. Boudreaux
Kelly D. Branham
Yihua Chang
James P. Dickerson
Erich E. Kathmann
Michael C. Kramer
Mark J. Logan

Pavneet S. Mumick
J. Kent Newman
Sheila L. Williamson

Undergraduate Students:

DeAnna L. Davis
James W. Denson
Cynthia G. Farmer
Steven C. Manning
Georgia Shafer
Paul M. Welch
D. Lane Windham

Post-Doctoral Associates:

Dr. Paul Ferguson

L. Other Funding

Leaf River Water Quality Study, Pat Harrison Waterway District, $40,000
Acid/Sugar Separation, Tennessee Valley Authority, $30,000
Polystyrene Study, Pennzoil, $16,340
Urea Study, International Fertilizer Development, $2,000
pH-Responsive Copolymers for Bioremediation Starter Grant, Exxon Chemical, $15,000
Support of Basic Research in Water-Soluble Polymers, Union Carbide Corporation, $30,000
Basic Research in Water-Soluble Polymers, Unilever Research U.S., Inc., $15,000
Basic Research in Water-Soluble Polymers, B. P. America, Inc., $19,000
Air Products Research Grant, Air Products and Chemicals, $52,000

PART II

Principle Investigators

Dr. Charles L. McCormick, Dr. Roger D. Hester
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Scientific Officers

Dr. JoAnn Milliken
Dr. Kenneth Wynne

Description of Project

Responsive synthetic copolymers are being tailored with specific microstructural features in order to elucidate drag reduction behavior and acoustical attenuation in aqueous media. Studies suggest that the major role of the polymer may be that of ordering the solvent in the immediate vicinity of the macromolecular coil. The key to varying fluid response under flow conditions lies in synthesizing specific polymer microstructures by appropriate monomer incorporation. Resulting microphase separation appears to alter solvation characteristics upon extension in fluid flow. New methods of data analysis allow for the first time direct comparisons of polymer type by assessing drag reduction efficiency as a function of polymer volume fraction. A master curve has been developed from this approach which yields an extensibility parameter suggested by a number of theoretical drag reduction models. Dynamic light scattering studies and photophysical techniques are being employed to study microphase organization. Rotating disk rheological measurements are being used to study drag reduction.

Significant Results During the Last Year

During the past year, focus has been placed on microstructurally tailored systems with ampholytic and hydrophobic moieties situated strategically along the macromolecular backbone. Among the polyampholytes, the zwitterionic polymers are the most efficient drag reducers. Their unique ability to switch between intramer and intramolecular ionic associations probably provides a better mechanism for turbulent energy dissipation. The high charge density polyampholytes show the poorest drag reduction efficiency due to very strong intramolecular ionic associations. The low charge density polyampholytes show intermediate efficiency in drag reduction. A

polyampholytic copolymer based on 3-(2-acrylamido-2-methylpropane-dimethyl-ammonio)-1-propanesulfonate and a hydrophobically associating copolymer based on diacetone acrylamide have drag reducing properties significantly superior to conventional polymers, i.e., poly(ethylene oxide) and homopolyacrylamide. Both these copolymers show increased drag reduction efficiency in salt solutions as compared to that in fresh water.

Research Planned for Period June 1, 1992 - May 31, 1993

In the next year, we will continue to study microstructurally tailored systems showing intra- and intermolecular hydrophobic associations. Special emphasis will be placed on polymer-surfactant interactions and their effect on drag reduction. Hydrophobically modified polyelectrolytes will also be characterized for dilute solution properties including drag reduction behavior as a function of solvent ionic strength. Since zwitterionic polyampholytes have shown excellent drag reduction properties, new zwitterionic models are being synthesized for further study. Drag reducing polymers are also being attached onto rotating disks. These coatings are being used to control the release of drag reducing polymers from solid surfaces into aqueous media. When perfected, this release technique will yield a practical means of utilizing the drag reduction phenomenon.

Graduate Students and Post Doctoral Fellow Currently Working on Project

Chase Boudreaux
Kelly Branham
Yihua Chang
Jimmy Dickerson
Erich Kathmann
Michael Kramer
Pavneet Mumick
Kent Newman
Sheila Williamson
Dr. Paul Ferguson

PART III

COPOLYMERS FOR DRAG REDUCTION IN MARINE PROPULSION

The University of Southern Mississippi
Department of Polymer Science
Charles L. McCormick and Roger D. Hester

OBJECTIVES

- Synthesis of water-soluble copolymers with energy dissipative modes of action in shear fields
- Characterization of copolymer microstructure
- Study of dilute solution properties including associative properties
- Determination of rheological properties and the role of hydration in turbulent flow
- Development of surface-grafted and ablative coatings

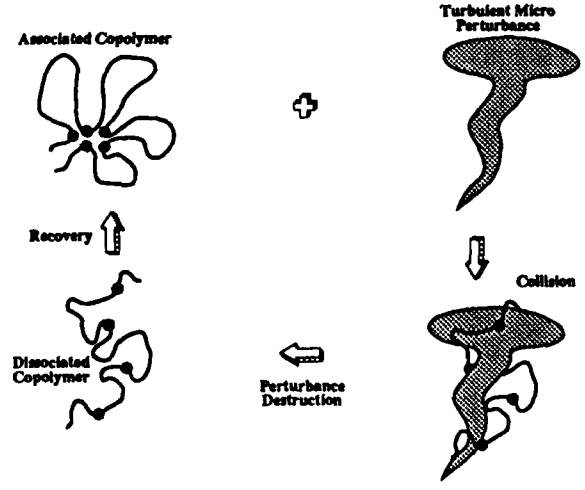
APPROACH

- Explore the drag reduction efficiency of carefully tailored copolymers with intra- and intermolecular associations in aqueous solutions
- Develop analytical procedures to relate drag reduction effectiveness to fundamental parameters of hydrodynamic volume and volume fraction
- Study polymer conformation and solvation utilizing fluorophore-labeled copolymers
- Develop copolymer coatings with controlled release properties

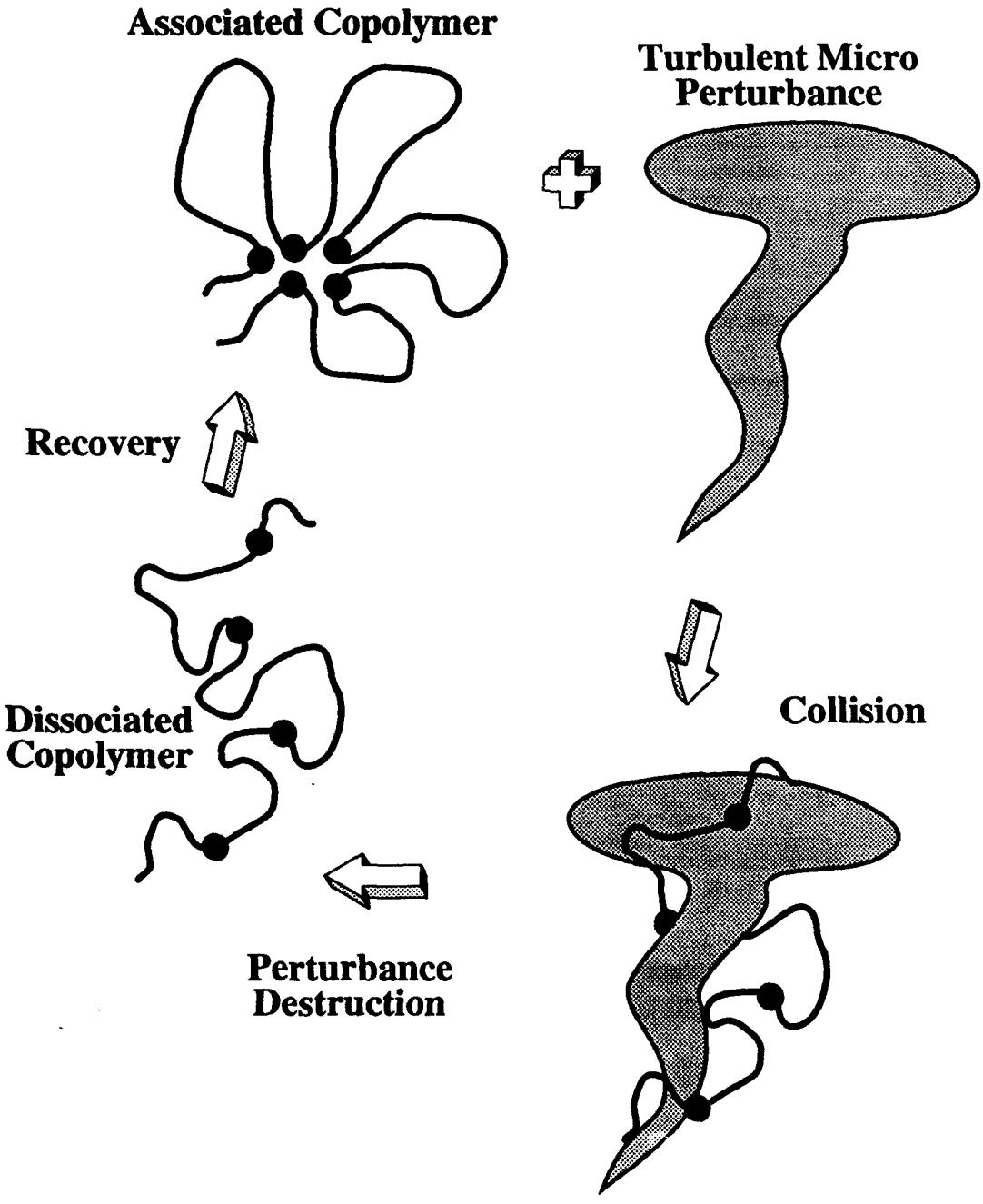
RELATED TECHNOLOGY

- The effects of aqueous drag reducing fluids on cavitation characteristics are under study. The extent to which acoustic detection and signature identification can be masked is of interest

REPRESENTATION OF DRAG REDUCTION MECHANISM



Reduction of Turbulence by Polymer-Perturbance Collision



DRAG REDUCTION PERFORMANCE OF SELECTED POLYMERS

Polymer Type*	Solvent	Rotating Disk Reynolds Number	Collision Efficiency
PEO	DI H_2O	675,000	150
PEO	DI H_2O	850,000	120
PEO	0.514M NaCl	675,000	290
PEO	0.514M NaCl	850,000	160
PAM	DI H_2O	675,000	600
PAM	DI H_2O	850,000	410
PAM	0.514M NaCl	675,000	457
PAM	0.514M NaCl	850,000	324
DAPS-10	DI H_2O	675,000	1060
DAPS-10	DI H_2O	850,000	621
DAPS-10	0.514M NaCl	675,000	1070
DAPS-10	0.514M NaCl	850,000	670
DAAM-35	0.514M NaCl	520,000	1600

*PEO—polyethylene oxide (Polyox WSR-N-60K)
PAM—polyacrylamide (Magnifloc 900N)
DAPS-10—3-(2-acrylamido-2-methylpropane-dimethylammonio)-1-propanesulfonate
DAAM-35—diacetone acrylamide

RESEARCH HIGHLIGHTS

Responsive Microphase Copolymer Fluids for Drag Reduction

A research team headed by Drs. Charles L. McCormick and Roger D. Hester from The University of Southern Mississippi is developing a series of responsive copolymers for utilization in drag reduction and acoustical attenuation applications. The key to responsive fluid behavior under flow conditions lies in microstructural organization of mers along the copolymer backbone and changes in solvation characteristics upon extension. A new method of data analysis from rotational disk flow and tube flow experiments allows determination of drag reduction efficiency as a function of volume fraction. Data analysis is based on a new kinetic model for drag reduction. Turbulence reduction is brought about by polymer collision with fluid perturbances. The probability of collision is dependent upon the volume fraction of polymer and the perturbance level produced by the flow field. Drag reduction results from the elimination of fluid perturbances. During collision, copolymers having superior drag reduction behavior are more efficient in eliminating perturbances. Efficiency is related to copolymer extensibility properties which are controlled by polymer microphase organization. The most efficient polymers made to date are a polyampholytic copolymer, DAPS-10, and a hydrophobically associating copolymer, DAAM-35.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1991	Journal article

4. TITLE AND SUBTITLE
Size Exclusion Chromatography of High Molecular Weight Water-Soluble Polymers

5. FUNDING NUMBERS
C: N00014-89-J-1893

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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8. PERFORMING ORGANIZATION REPORT NUMBER
91-92-1

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Avenue
Arlington, VA 22217

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Published in J. Applied Polymer Sci., 1991, 43, 1987-1990

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*
See attachment

14. SUBJECT TERMS

15. NUMBER OF PAGES
4

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Unlimited

Size-Exclusion Chromatography of High Molecular Weight Water-Soluble Polymers

ABBAS M. SAFIEDDINE and ROGER D. HESTER*

Department of Polymer Science, The University of Southern Mississippi, Hattiesburg, Mississippi 39406-0076

SYNOPSIS

A preparative-scale, aqueous size-exclusion chromatography system was constructed for fractionation of large molecular weight polymers. Calibration of molecular weight to elution volume was accomplished without polymer standards by using an eluent viscosity detector in series with a refractometer. The system was found to have a hydrodynamic size-separation resolution that ranged from 500 to 3500 Å.

INTRODUCTION

Size-exclusion chromatography (SEC) is a characterization technique useful in the analysis of polymers in both organic and aqueous media. Polymer molecules elute from an SEC column according to their hydrodynamic size. To obtain an SEC system capable of measuring molecular weight (MW), one must calibrate elution volume as a function of hydrodynamic size. This is usually accomplished by plotting several polymer standards of known MW or hydrodynamic size versus elution volume. Thus, construction of an SEC calibration curve requires polymer standards. Standards are readily obtainable for low MW polymers. However, high MW standards over 1 million daltons for aqueous SEC are unavailable.

A detection problem also exists with high MW polymers. To prevent overloading of an SEC column, the sample concentration and total fluid volume injected must be limited. Injected concentrations must be reduced as sample hydrodynamic size increases. Thus, polymer detection in the SEC eluent becomes increasingly difficult with increasing MW. When this problem of low eluent polymer concentration is coupled with the unavailability of polymer standards, the task of calibrating an aqueous SEC system becomes formidable.

We have implemented an eluent viscosity detector similar to that constructed by Ouano and Baker[1] and others.[2] The combination of a viscodetector with a differential refractometer has enabled the calibration of an aqueous SEC system by a single injection of a polydisperse high MW polymer sample. The calibration technique outlined in this paper simplifies the use of aqueous SEC to measure MW distributions of high MW polymers.

SEC SYSTEM

A preparative SEC system was constructed as shown in Figure 1. A Waters 510 dual piston pump equipped with pulse dampeners was used to draw degassed DI water from a 20 L Pyrex reservoir and maintain the flow rate at 5.2 mL/min. The aqueous stream was passed through two large 5.75 cm-inside-diameter-columns connected in series and having a total length of 200 cm. The columns were packed with TSK-GEL HW-75F, a semirigid gel that has good chemical and physical stability and high resolution in separating large water-soluble polymers. A viscodetector and a differential refractive index detector (HP-1037A) were connected in series to measure eluent viscosity and polymer mass, respectively. The viscodetector measured the eluent pressure drop across a 0.127 cm-diameter stainless steel tube having a length of 212 cm by using a Validyne DP-15 pressure transducer equipped with a 1.25 psi pressure plate. The tubing was immersed in a water bath maintained at 30.0°C. The analog signals from both detectors were input into an IBM-PC compatible computer through an analog-to-digital (A/D) converter (ACPC-16, Strawberry Tree Computers, CA).

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 43, 1987–1990 (1991)
 CCC 0021-8995/91/111987-04$04.00

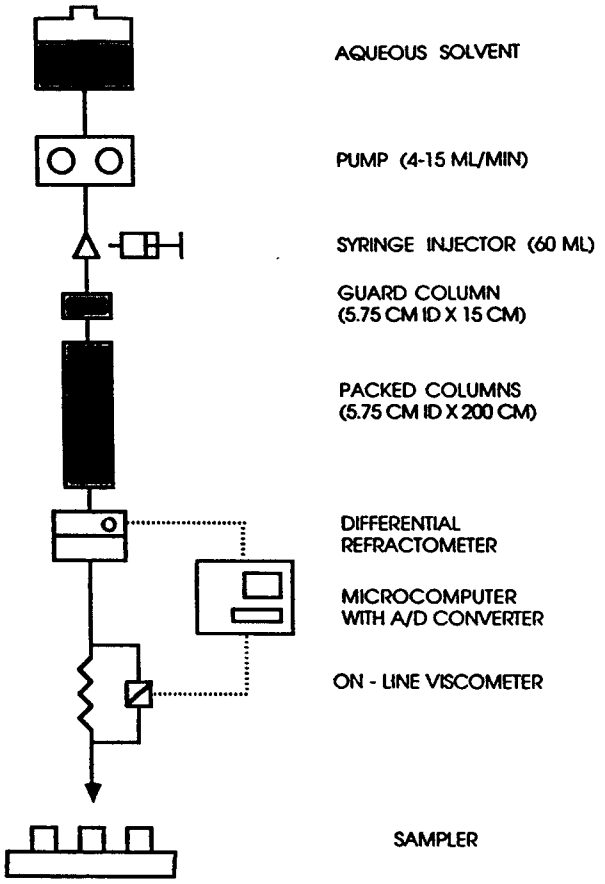

Figure 1 Preparative GPC system.

The system has the following advantages over conventional analytical scale SEC systems:

- Corrections for fluid volume between detectors is not necessary. The volume between detectors is very small and becomes insignificant at the high flow rates used in the larger-scale preparative SEC system.
- The data are acquired at 1–2 minute intervals and the value stored is the average during the period. A date file consists of several hundred average values. Therefore, the system has minimal sensitivity to small flow-rate fluctuations.
- Because of the preparative nature of the system and the presence of damping coils, fluid pressure pulsations from the pump are significantly damped. There is no further need to "smooth" the raw signal from the on-line differential pressure transducer.

DATA ANALYSIS

The eluent viscosity detector can be used to determine the instantaneous specific viscosity, η_{sp_i}, of a polymer solution leaving the size-exclusion column. Equation (1) was employed to perform a fluid specific viscosity calculation from the pressure drop across the viscosity detector tube. This relationship in valid for the steady laminar volumetric flow through the viscosity detector tube. Under these conditions, the pressure drop of the polymer solution across the tube, ΔP_i, is proportional to the solution viscosity. When only solvent is flowing through the tube, the pressure drop, ΔP_0, is proportional to the solvent viscosity:

$$\eta_{sp_i} = (\Delta P_i - \Delta P_0)/\Delta P_0 \qquad (1)$$

The signal from the refractive index (RI) detector can be used to calculate the concentration of polymer, C_i, in each equal volume aliquot of eluent, ΔV_e:

$$C_i = mS_i/(\Delta V_e \sum S_i) \qquad (2)$$

In Equation (2), "m" is the total mass of polymer sample injected, S_i is the RI signal with base line subtracted at aliquot i, and $\sum S_i$ is the sum of all RI signals taken in a chromatogram when polymer is eluting. This relationship assumes that the total mass of sample injected is proportional to the area of the chromatogram obtained when a plot of elution volume versus RI signal is constructed.

Sample intrinsic viscosity is the ratio of specific viscosity to concentration as the concentration approaches zero. The polymer solution eluting the SEC are very dilute; thus, the ratio of instantaneous specific viscosity to instantaneous concentration closely approximate an instantaneous apparent intrinsic viscosity, $[\eta]_{app_i}$:

$$[\eta]_{app_i} \cong \eta_{sp_i}/C_i \qquad (3)$$

The apparent intrinsic viscosity, calculated using eq. (3), must be corrected for the shear thinning or pseudoplastic flow behavior of a dilute polymer solution.[3] A true intrinsic viscosity must be measured at low flow conditions that approach a zero shear rate in the tube. Estimation of the true intrinsic viscosity from the apparent intrinsic viscosity, which was measured at 400 s^{-1} tube shear rate ($\dot{\gamma}$), was accomplished using a modification of a dilute polymer solution rheological equation developed by Bueche[4]:

$$[\eta]_{app_i} = [\eta]_{true_i} - \sqrt{12\epsilon\eta_s/(\pi RTK^{1/a})}\,[\eta]_{true_i}^{3a+1/2a}\sqrt{\dot{\gamma}} \qquad (4)$$

In eq. (4), ϵ is a constant having a value of 0.694,

T is the absolute temperature, R is the gas constant, η_s is the solvent viscosity, and "a" and "K" are the Mark–Houwink constants for the polymer–solvent system. All the parameters enclosed by a square root are known. Thus, $[\eta]_{\text{true}_i}$ can be calculated from measured $[\eta]_{\text{app}_i}$ values by using Newton's iterative method. The Bueche relationship has been subject to some controversy regarding validity[5]; however, in this application, the shear correction produced true intrinsic viscosity values that were no more than 10% greater than the apparent intrinsic viscosity. Also as expected, the correction for the applied shear rate, 400 s^{-1}, was insignificant for solutions of low MW polymers.

The overall polymer sample intrinsic, $[\eta]_t$, was calculated from the sum of all fraction contributions:

$$[\eta]_t = \sum (C_i[\eta]_{\text{true}_i}\Delta V_e)/\sum (C_i\Delta V_e) \quad (5)$$

CALIBRATION

The instantaneous hydrodynamic diameter of a random coil polymer in each aliquot, d_i, can be estimated from the knowledge of the instantaneous true intrinsic viscosity[6]:

$$d_i = 5([\eta]_{\text{true}_i}M)^{1/3} \quad (6a)$$

$$d_i = 5([\eta]^{a+1}_{\text{true}_i}/K)^{1/3a} \quad (6b)$$

In eq. (6a), the molecular hydrodynamic diameter is expressed in angstroms and the intrinsic viscosity is in units of deciliters per gram. As indicated in eq. (6b), Mark–Houwink "K" and "a" values can be used to relate hydrodynamic diameter directly with intrinsic viscosity.

The fraction of packing micropore volume penetrated by a molecule eluting at fluid volume, V_e, or the partition coefficient is given by

$$K_i = (V_{e_i} - V_0)/(V_t - V_0) \quad (7)$$

In eq. (7), K_i is the partition coefficient associated with V_{e_i}, the instantaneous elution volume. V_0 is the packing interstitial volume, and V_t is the total packing permeation volume. V_0 and V_t values can be experimentally obtained.

From the above relationship, an SEC calibration plot of hydrodynamic diameters versus the natural logarithm of the partition coefficient can now be constructed.[7,8] A semilog calibration plot that shows the relationship between natural logarithm of partition coefficient versus the hydrodynamic diameter is expected to be approximately linear.[9]

Furthermore, a continuous SEC calibration plot can be constructed by injecting a single polydispersed sample whose Mark–Houwink "K" and "a" values are known. After calibration, an uncharacterized random coil polymer can be injected into the SEC system and the RI signal obtained versus time (or equivalent elution volume) can be converted to an MW distribution using the calibration curve. From the known calibration curve, the hydrodynamic diameter corresponding to any elution volumn (or partition coefficient value) can be established. As shown by eq. (8), each hydrodynamic diameter has an MW that can be calculated by a rearrangement of eq. (6a):

$$M_i = \frac{d_i^3}{125[\eta]_{\text{true}_i}} \quad (8)$$

As shown by eq. (9), the relative number of molecules that parallel each molecular weight, N_i, can be calculated from the concentration, C_i, obtained from the RI signal [see eq. (2)]:

$$N_i = C_i\Delta V_e/M_i \quad (9)$$

Utilizing the above methodology, a molecular weight distribution (MWD) showing N_i versus M_i can be constructed for any unknown polymer sample.

RESULTS AND DISCUSSION

Figure 2 displays two calibration curves obtained experimentally using polyethylene oxide and polyacrylamide samples. Both curves are very similar and show the expected linear relationship between Ln(K) and d. The deviation of the polyacrylamide curve in the smaller hydrodynamic size region and the slight curvature are probably due to the inability of a single set of Mark–Houwink values to relate accurately MW to intrinsic viscosity at the extremes of an MWD. The Mark–Houwink values used were those recommended for polymers having very high MWs (Table I).

The calibration curves show that the separation of water-soluble macromolecules having hydrodynamic sizes up to 3500 Å can be accomplished. Thus, coupling of RI and viscosity detector information has enabled rapid calibration of SEC systems with polydispersed polymer samples. After calibration, the procedures explained in this paper can be used to obtain MWD information on random coil polymers and copolymers that have unknown Mark–Houwink "K" and "a" values.

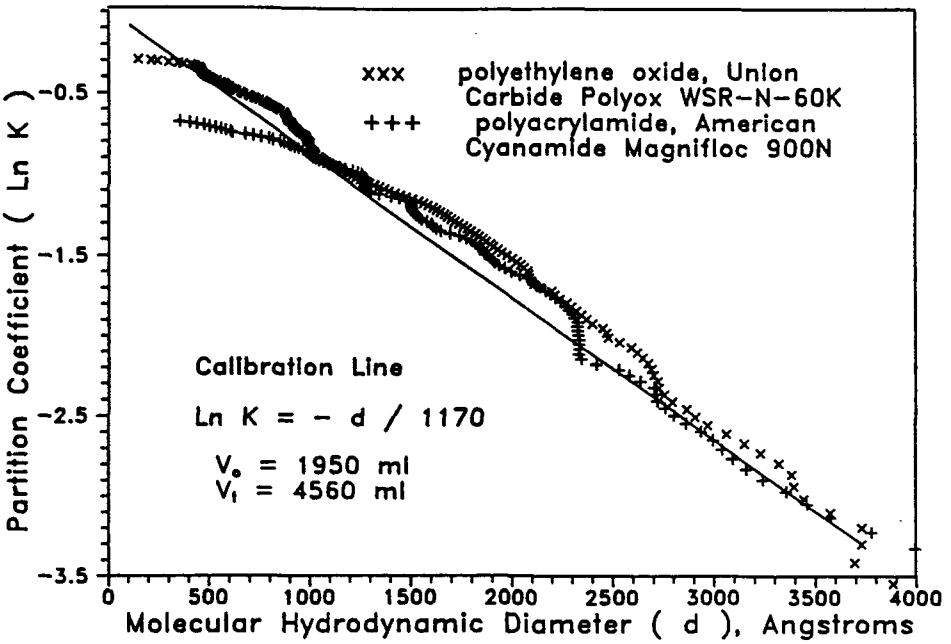

Figure 2 Calibration curves for the aqueous SEC system.

Mark–Houwink "K" and "a" values can be estimated for polymers by having a calibration curve. This can be accomplished by fitting d_i versus K_i values obtained using a given set of Mark–Houwink constants to the calibration curve. Subsequent adjustment of the "K" and "a" values can be made until a best fit to the calibration curve is obtained. The reader is referred to a recent publication by Price et al. for the details of a similar procedure.[11]

SUMMARY

A chromatographic system capable of separating high MW water-soluble polymers has been constructed and calibrated. Calibration was achieved by coupling data from both refractive index and viscosity chromatograms using polydispersed samples. The SEC system was found to have a resolution that ranged from 500 to 3500 Å in hydrodynamic diameter. The system has been successfully utilized in fractionating polyethylene oxide and polyacrylamide. The SEC system has the ability to fractionate polydisperse water-soluble polymers in large volumes of narrow MW fractions, enabling the study of rheological and dilute solution flow behavior on aqueous polymers with narrow MWD.

Table I Mark–Houwink Constants for Polyacrylamide (PAM) and Polyethylene Oxide (PEO) at 30°C

Polymer	a value	K value $\times 10^5$ (dL/g)
PAM[a]	0.80	6.31
POE[a]	0.78	12.5

[a] Ref. 10.

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Received October 20, 1990
Accepted January 23, 1991

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1992	Journal article

4. TITLE AND SUBTITLE
Water Soluble Copolymers. 37. Synthesis and Characterization of Responsive Hydrophobically Modified Polyelectrolytes

5. FUNDING NUMBERS
C: N00014-89-J-1893

6. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NUMBER
91-92-2

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Avenue
Arlington, VA 22217

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Published in Macromolecules, 1992, 25(4), 1201-1206

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)
See attachment

14. SUBJECT TERMS

15. NUMBER OF PAGES
6

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Unlimited

Macromolecules

Volume 25, Number 4 February 17, 1992

Water-Soluble Copolymers. 37. Synthesis and Characterization of Responsive Hydrophobically-Modified Polyelectrolytes

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Received June 18, 1991; Revised Manuscript Received September 30, 1991

ABSTRACT: Hydrophobically-modified, water-soluble polyelectrolytes have been prepared by a micellar technique from acrylamide, *n*-decylacrylamide, and a third monomer, sodium 3-acrylamido-3-methylbutanoate, sodium acrylate, or sodium 2-acrylamido-2-methylpropanesulfonate. These terpolymers exhibit rheological behavior dependent upon the terpolymer composition, nature of the charged monomer, ionic strength, and pH. Although the hydrophobic monomer is incorporated in low concentration, the associative effects are profound, with some compositions maintaining high viscosity in NaCl concentrations of up to 0.514 M. Hydrophobic associations in terpolymers with the carboxylate anion are stronger than those in structurally analogous terpolymers containing the sulfonate anion, especially at high NaCl concentrations. Within the carboxylate series, copolymers with the carboxylate group closer to the polymer backbone exhibit greater viscosity increases with added electrolyte above the critical overlap concentration, C^*. Presence of carboxylate or sulfonate groups farther from the macromolecular backbone disrupts to a greater extent such hydrophobic associations.

Introduction

Studies in our laboratories have focused on developing macromolecules that can maintain or increase the viscosity of aqueous solutions in the presence of mono- or multivalent electrolytes.[1-10] Such polymers may have important commercial applications in enhanced oil recovery, drag reduction, flocculation, superabsorbency, and personal care and coatings formulations. Hydrophilic polymers containing a small number of water-insoluble groups can undergo microphase separation and associations in aqueous solution.[11-17]

Recent work by our research group involved the synthesis and characterization of copolymers of acrylamide with *n*-alkylacrylamides with alkyl lengths of 8, 10, and 12 carbons. These polymers exhibit microheterogeneous associative behavior with the incorporation of <1 mol % of *n*-alkylacrylamide.[18,19] While such copolymers yield high-viscosity solutions in the presence of added electrolytes above a critical concentration, they are difficult to hydrate from the dry state. To enhance dissolution and provide potential responsiveness to salt or pH changes, terpolymers containing acrylamide (AM), 0.5 mol % of *n*-decylacrylamide (C10AM) as the hydrophobic monomer, and sodium 3-acrylamido-3-methylbutanoate (NaAMB), sodium acrylate (NaA), or sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) were synthesized.[20-22] Two carboxylate monomers and one sulfonate monomer were selected to evaluate the differences in pK_B of pendent anions and to observe the influence of the distance of the charged group from the polymer backbone. Rheological properties were determined by low-shear viscometry in deionized water and sodium chloride solutions.

Experimental Section

Materials. Acrylamide (AM), obtained commercially from Aldrich Chemical Co., was recrystallized twice from acetone, dried under vacuum, and stored in a desiccator prior to use (mp 81–84 °C). Acrylic acid, also obtained from Aldrich, was purified by vacuum distillation in the presence of cupric sulfate to remove inhibitor prior to use. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) was obtained from Fluka Chemical Co. and recyrstallized twice from a mixture of methanol and 2-propanol. *n*-Decylacrylamide[18] (C10AM) and 3-acrylamido-3-methylbutanoic acid (AMBA)[22] were synthesized and purified by previously reported methods. The monomers (Figure 1) were polymerized in their sodium salt forms.

Potassium persulfate from J. T. Baker Co. was recrystallized twice from deionized water prior to use. Sodium dodecyl sulfate, received from Aldrich Chemical Co., was used without further purification. Reagent grade sodium chloride from Fisher Scientific Co. was used without further purification. All aqueous solutions were prepared using deionized water.

Polymer Synthesis. The incorporation of water-soluble and water-insoluble monomers into the polymer backbone was accomplished by a micellar polymerization method.[16] In this technique use of a surfactant is necessary to solubilize the hydrophobic monomer. Sodium dodecyl sulfate (SDS) was chosen as the surfactant in this instance. Each reaction was conducted in a 500-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet, and condenser. The appropriate amount of ionizable monomer was placed in deionized water, and the pH was adjusted to 9 with NaOH to form the water-soluble salt. This amount was recorded and the

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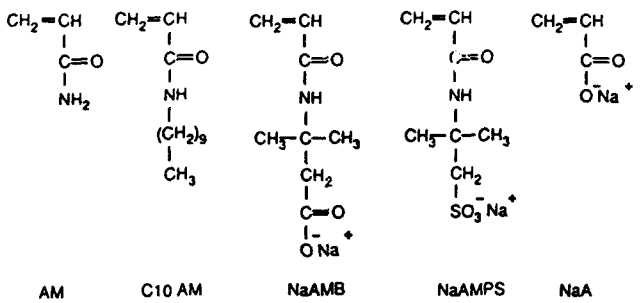

Figure 1. Structures of monomers used to prepare terpolymers.

Table I
Copolymer Comparison of C10AM Terpolymers from Elemental Analysis Neglecting C10AM

sample	feed ratio M_1:M_2[a]	elem anal. % C	elem anal. % N	polym comp, mol % M_1	polym comp, mol % M_2
NaAMPS-40[b]	59.5:40	39.39	10.12	68.8	31.2
NaAMPS-25	74.5:25	42.01	11.18	65.6	34.4
NaAMPS-10	89.5:10	45.17	14.37	83.7	16.3
NaAMPS-5	94.5:5	41.25	14.64	92.5	7.5
NaAMB-40	59.5:40	48.90	12.34	67.0	33.0
NaAMB-25	74.5:25	45.67	12.80	76.9	23.1
NaAMB-10	89.5:10	48.80	16.17	89.6	10.4
NaAMB-5	94.5:5	45.85	16.09	93.9	6.1
NaA-40	59.5:40	41.50	11.94	73.9	26.1
NaA-25	74.5:25	42.43	13.19	79.7	20.3
NaA-10	89.5:10	45.00	15.33	87.2	12.8
NaA-5	94.5:5	45.11	16.11	94.4	5.6

[a] M_1 = AM; M_2 = NaAMPS, NaAMB, or NaA. [b] Feed composition of ionizable monomer.

solution diluted to a final volume of 230 mL (13.0 mol). The acrylamide monomer was dissolved in this solution, placed in a round-bottom flask, and was deaerated with purified nitrogen for 30 min. Surfactant (7.93 g, 2.8×10^{-2} mol) and 0.109 g (5.2×10^{-4} mol) of C10AM monomer were then added, and the solution was heated to 50 °C with stirring under a nitrogen atmosphere. Potassium persulfate (0.005 g, 1.8×10^{-5} mol) dissolved in 5 mL of deionized water was added for a total water volume of 235 mL and a total monomer concentration of 0.44 M. The polymerizations were conducted for 4–6 h followed by dilution with an equal amount of water and precipitation into acetone. The polymers were washed extensively in acetone and then dried under vacuum for 24 h. Molecular weights for four acrylamide homopolymers prepared under the above conditions were determined to be from 1.0×10^6 to 1.5×10^6 by light scattering. Associative interactions precluded meaningful molecular weight measurements for the hydrophobically-modified terpolymers; however, molecular weights would be expected to be in the same range.

Polymer Composition. Elemental analyses for carbon, hydrogen, and nitrogen content of the terpolymers were conducted by M-H-W Laboratories of Phoenix, AZ. In addition, sulfur analyses of representative samples (of polymers not containing NaAMPS) were performed to confirm the absence of residual surfactant (Table I). The low amount of C10AM incorporated into the polymer could be neglected in elemental analysis calculations without inducing significant error.

Viscometry. Stock solutions of sodium chloride (0.085, 0.170, 0.257, 0.342, and 0.514 M) were prepared by dissolving the appropriate amount of salt in deionized water contained in volumetric flasks. Polymer samples were dissolved by gentle shaking on an orbital shaker for 14 days to allow complete hydration before further dilutions of these stock solutions were made.

Viscosity experiments were conducted on the Contraves LS 30 low-shear rheometer at a shear rate of 6 s^{-1} at 30 °C. The upper limit of the Contraves is 250 cP at a shear rate of 6 s^{-1}. Several polymers exceeded this value in the concentration range investigated. These polymer solutions were gels, and a value of 250 cP was assigned to them for graphical purposes.

Results and Discussion

Electrostatic interactions and hydrophobic effects for copolymers of the type prepared in this study may lead to microheterogeneous phase separation of important consequence in aqueous solution. The electrostatic interaction of carboxylate or sulfonate groups along the backbone generally increase the hydrodynamic volume while hydrophobic moieties aggregate in aqueous solution by intramolecular (closed) or intermolecular (open) associations dependent upon polymer microstructure, concentration, and molecular weight. Proper selection of synthetic conditions can lead to technologically important systems responsive to changes in pH or electrolyte concentration.

Feed Composition. Three series of terpolymers were prepared by a modified micellar polymerization technique reported in the patent literature by Turner, Siano, and Bock.[16] The reaction conditions (Table I) were chosen to have feed compositions of 0.5 mol % of the hydrophobic monomer C10AM, specified (5, 10, 25, and 40 mol %) concentration of the anionic monomer, NaAMB, NaAMPS, or NaA, and the remainder AM. Our initial objectives were to achieve an associative viscosifier with properties of the uncharged C10AM/AM copolymer previously prepared[19] but with pH or electrolyte responsiveness. Additionally, it was our desire to assess the roles of the carboxylate and sulfonate groups on hydrophobic domain disruption.

Terpolymer Composition. Data from elemental analysis show agreement between feed ratios and copolymer composition up to 20 mol % of the anionic monomer (Table I). Above 20 mol %, the incorporation likely decreases as electrostatic repulsions between structopendent charged groups of the growing polymer chain and charged monomer units become significant. While the incorporation of C10AM cannot be determined by conventional methods such as elemental analysis or NMR, Valint et al.[24] have shown >85% incorporation of a chromophore-labeled hydrophobic monomer by ultraviolet spectroscopy. Terpolymers with ionizable monomer feed compositions of 5 and 25 mol % are representative samples of a low-charge-density and a high-charge-density terpolymer, respectively. Terpolymers (Table I) are named according to the type and concentration of ionic monomer present. For example, the terpolymer with a feed composition of 0.5 mol % C10AM, 94.5 mol % AM, and 5 mol % NaAMB is referred to as NaAMB-5.

Solution Studies. Apparent viscosity (η_{app} in centipoise) is plotted as a function of polymer concentration (grams per 100 mL or g/dL) and of solution ionic strength ([NaCl]) in three-dimensional plots to clearly illustrate solution behavior. Reduced viscosity (η_{red} in deciliters per gram) is plotted as a function of polymer concentration for each polymer sample at specific NaCl concentrations to further illustrate rheological changes (Figures 2–7).

NaAMPS Terpolymers. Both NaAMPS-5 and NaAMPS-25 show typical polyelectrolyte behavior at low solution ionic strengths (Figures 2 and 3). The apparent viscosities of both systems are high at low ionic strength, characteristic of typical hydrated polyelectrolytes. Viscosity then decreases with increasing ionic strength as the charged groups are shielded by the addition of NaCl. However, above a critical polymer concentration (C^*), η_{app} and η_{red} of NaAMPS-5 increase with increasing solution ionic strength above 0.26 M NaCl, atypical of traditional polyelectrolytes (Figure 2). The low-charge-density polymer (Figure 2b) shows a linear increase in η_{red} only for the low ionic strength solution. At higher ionic strength, η_{red}

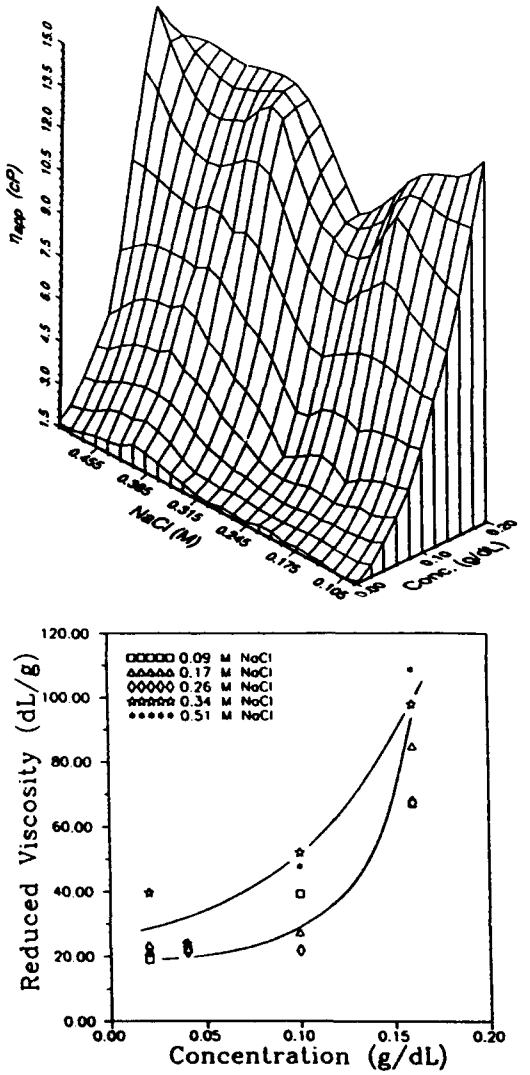

Figure 2. (a, Top) η_{app} as a function of polymer concentration and solution ionic strength for the NaAMPS-5 terpolymer. (b, Bottom) η_{red} versus polymer concentration for the NaAMPS-5 terpolymer at five different solution ionic strengths.

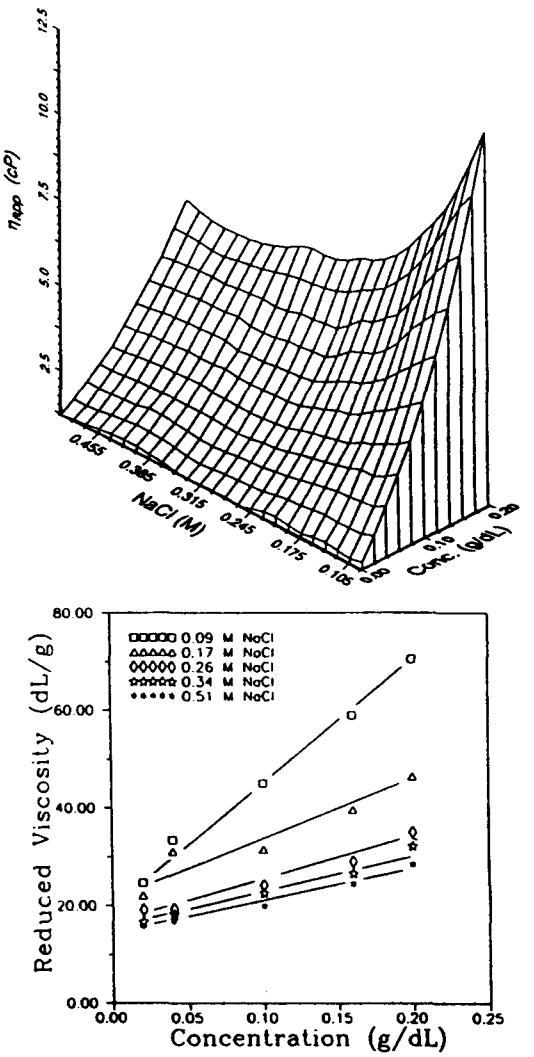

Figure 3. (a, Top) η_{app} as a function of polymer concentration and solution ionic strength for the NaAMPS-25 terpolymer. (b, Bottom) η_{red} versus polymer concentration for the NaAMPS-25 terpolymer at five different solution ionic strengths.

increases rapidly, indicative of interpolymer associations. The high-charge-density NaAMPS-25 polymer shows linear behavior at all ionic strengths investigated; apparently the increased charge density effectively prevents hydrophobic aggregation (Figure 3) by disrupting water structure ordering necessary for associative thickening behavior.

NaAMB Terpolymers. The NaAMB terpolymers exhibit unusual behavior as demonstrated by an increase in apparent viscosity with increasing solution ionic strength (Figures 4a and 5a). The NaAMB-5 terpolymer does not show associative behavior at NaCl concentrations less than 0.17 M. The electrostatic repulsions of the NaAMB groups are sufficient to prevent interpolymer aggregation through hydrophobic associations. At 0.26 M NaCl, however, a rapid increase in apparent viscosity is observed above 0.10 g/dL, indicative of associative behavior. In 0.51 M NaCl, no further aggregation occurs above 0.10 g/dL. However, because the coil is further collapsed by the large excess of NaCl, apparent viscosity is lower than that of the polymer in 0.34 M NaCl. This also is clearly illustrated in the reduced viscosity plots for the NaAMB-5 polymer, where linear behavior is observed only for the 0.17 M NaCl solution. Above 0.17 M NaCl, η_{red} again increases nonlinearly, indicating associative behavior (Figure 4b).

The NaAMB-25 terpolymer (Figure 5) behaves in a different manner from NaAMB-5. The higher polymer charge density results in a more expanded coil at low solution ionic strength. Initially, coil collapse due to ionic shielding occurs with increasing NaCl concentration followed by an increase in viscosity. The NaAMB-25 curve does not exhibit the maximum seen in the low-charge-density polymer system, suggesting insufficient electrolyte to effectively reduce charge–charge repulsions. Reduced viscosity solution behavior is linear for the high-charge-density NaAMB-25 polymer up to a concentration of 0.15 g/dL. Above this concentration the polymers associate and η_{red} increases exponentially.

NaA Terpolymers. An initial decrease and the leveling of apparent viscosity with increasing ionic strength at high concentration are observed for NaA-5 (Figure 6a). The polymer has nonlinear reduced viscosity solution behavior at all ionic strengths (Figure 6b). The higher-charge-density polymer (NaA-25) has low viscosity in low ionic strength solution, and apparent viscosity rapidly increases with increasing salt solution to form gels with viscosities greater than 250 cP (Figure 7a). Similar behavior is seen in the η_{red} plot; viscosity increases even more rapidly at higher ionic strength (Figure 7b).

Comparison of the NaAMPS, NaAMB, and NaA Terpolymers. NaAMPS terpolymers demonstrate associative behavior only at low charge densities and

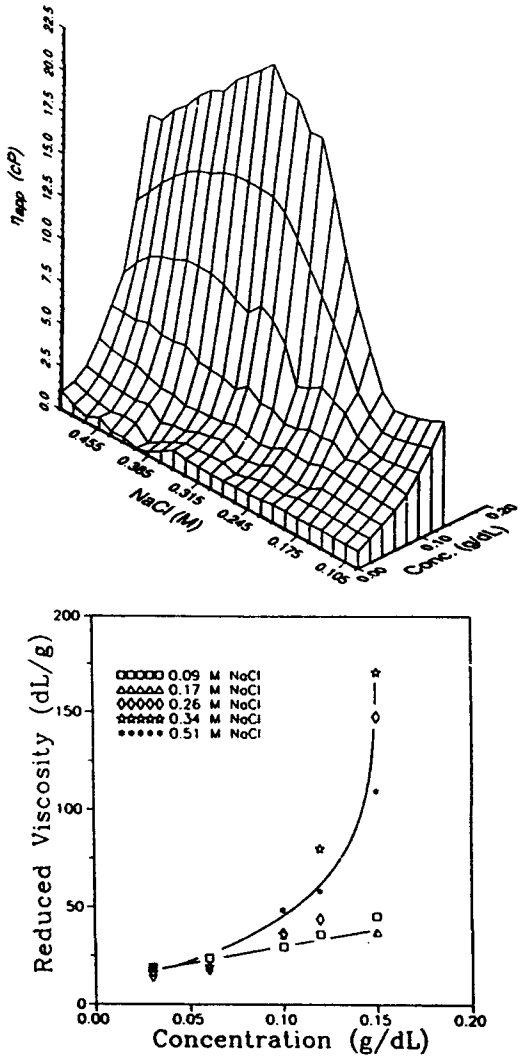

Figure 4. (a, Top) η_{app} as a function of polymer concentration and solution ionic strength for the NaAMB-5 terpolymer. (b, Bottom) η_{red} versus polymer concentration for the NaAMB-5 terpolymer at five different solution ionic strengths.

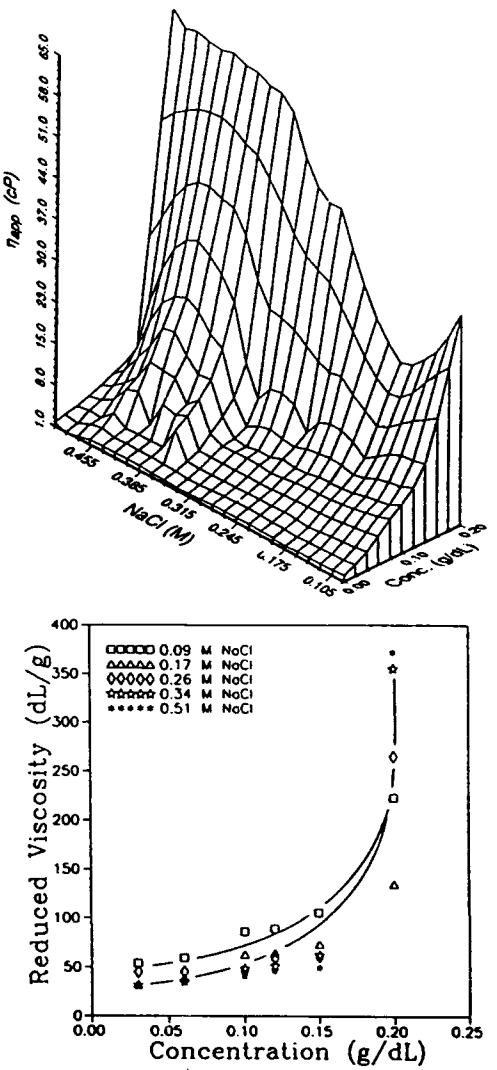

Figure 5. (a, Top) η_{app} as a function of polymer concentration and solution ionic strength for the NaAMP-25 terpolymer. (b, Bottom) η_{red} versus polymer concentration for the NaAMP-25 terpolymer at five different solution ionic strengths.

moderate-to-high ionic strength. However, for the NaAMB and NaA terpolymers, apparent viscosity increases linearly with sample concentration up to a critical value of solution ionic strength. Above this NaCl molarity, the viscosity exponentially increases with polymer concentration, indicative of intermolecular hydrophobic association. The salt concentration necessary for this transition is higher for the NaAMB polymer than for the NaA polymer. It is also apparent that the terpolymers containing NaA have much higher viscosities than the other systems investigated.

Conceptual Models. At low ionic strength and high charge density, the electrostatic repulsive forces dominate the polymer solution behavior and all the polymers act as polyelectrolytes with similar viscosities. Armstrong and Strauss[26] have depicted a typical polyelectrolyte as an extended chain with the ionic atmosphere projecting out radially to a distance on the order of the Debye–Hückel shielding length (κ^{-1}) where for a 1:1 simple electrolyte $\kappa^{-1} = 0.304/I^{1/2}$ (e.g., for a 0.1 M NaCl solution $\kappa = 0.1$ nm). The entire chain may be envisioned as enclosed by a tube with an average diameter of $2\kappa^{-1}$. Even in excess electrolyte, where the chain may form a random coil, the local geometry may be represented by the above model if the radius of curvature is greater than $2\kappa^{-1}$.

The presence of pendent C10AM hydrophobic groups along the polymer backbone apparently changes the aqueous solution behavior from that of a typical polyelectrolyte at higher ionic strengths; the nonpolar *n*-decyl groups are excluded from the polar environment,[26] resulting in network formation. The onset value of interaction at low C^* values has yet to be explained; however, Israelachvili et al.[27,28] and Pashley et al.[29] have demonstrated long-range attractive interaction of crossed cylinders of hydrophobically-modified mica surfaces. They reported attractive forces 10–100 times stronger than expected van der Waals force over distances up to 10 nm. These forces decay exponentially with a force proportional to $\exp(-D/1.0)$.

In our terpolymer systems, as the charge density decreases and solution ionic strength increases, the electrostatic potential along the polymer chain decreases, allowing long-range hydrophobic attractions well below that of C^* for unmodified polyacrylamides.[19,20] Israelachvili has predicted aggregation for charged, hydrophobically-modified colloid particles where the Debye–Hückel parameter approaches the decay length of 1.0 nm for hydrophobic associations corresponding to a solution ionic strength for NaCl of 0.1 M.[28] This is consistent with our finding that significant associative behavior occurs only at ionic strengths greater than or equal to 0.17 M NaCl.

Strauss et al. observed similar behavior with poly(4-vinylpyridine) derivatives[31,32] hydrophobically modified

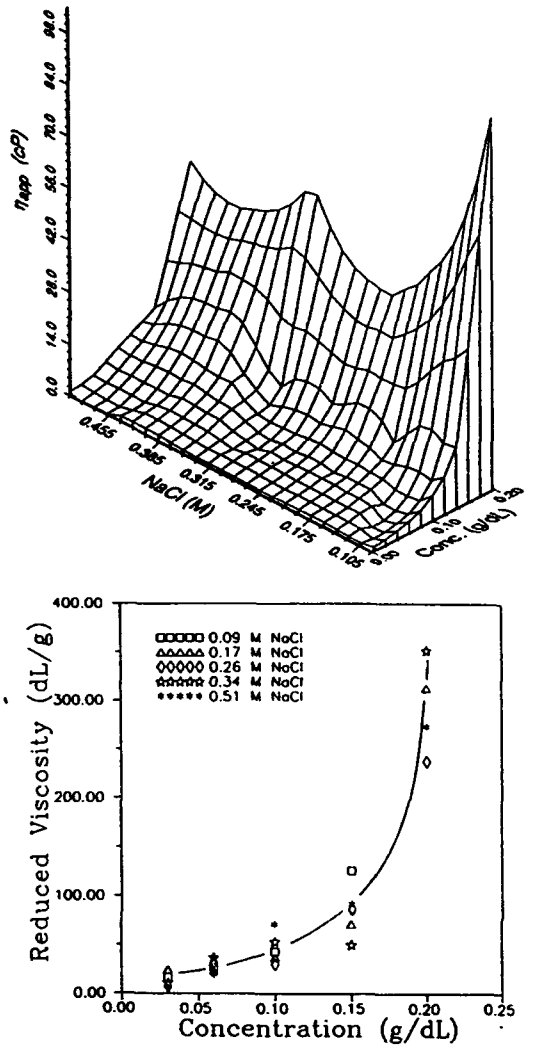

Figure 6. (a, Top) η_{app} as a function of polymer concentration and solution ionic strength for the NaA-5 terpolymer. (b, Bottom) η_{red} versus polymer concentration for the NaA-5 terpolymer at five different solution ionic strengths.

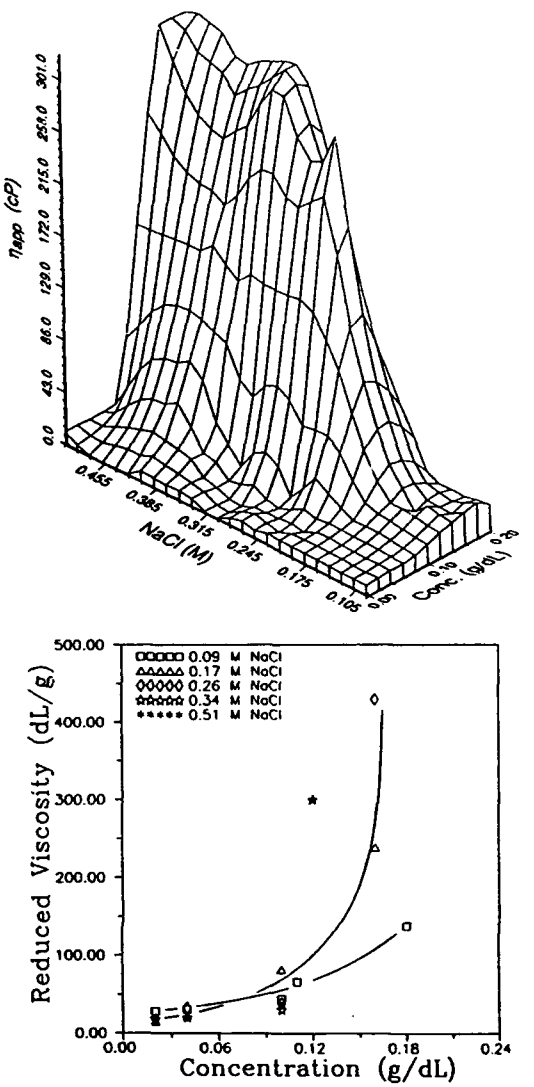

Figure 7. (a, Top) η_{app} as a function of polymer concentration and solution ionic strength for the NaA-25 terpolymer. (b, Bottom) η_{red} versus polymer concentration for the NaA-25 terpolymer at five different solution ionic strengths.

with ethyl and dodecyl side chains. Low hydrophobic group incorporation resulted in polymers that displayed intermolecular association above C^*; with increasing hydrophobic group incorporation, the polymers associated intramolecularly, resulting in polysoaps. Above a critical polymer concentration, sufficient hydrophobic groups were present to associate in either an inter- or an intramolecular fashion. The associations of bound hydrophobic groups were discussed in terms of a critical micelle concentration similar to that for small-molecule surfactants. At low dodecyl group incorporation, an insufficient number of hydrophobic groups are present on any individual polymer chain to form a stable ensemble. When a critical polymer concentration is reached, the polymer chains associate to form an intermolecular network in the aqueous system.

The association of polymer chains results in a rapid increase in apparent molecular weight (M_{app}). Below this critical molecular weight, η_{app} and η_{red} increase in a linear fashion, and reduced viscosity as a function of concentration may be plotted according to the Huggins equation.[33] Above a critical M_{app} (M_c) viscosity increases exponentially instead of linearly[34] as seen by the increases in both apparent and reduced viscosity (Figures 2–7).

The terpolymers containing NaAMPS are the least affected by changing ionic strength, reflecting the soft nature of the sulfonate anion. The carboxylate anions of NaAMB and NaA polymers, on the other hand, show aggregation as ionic shielding causes collapse of the Debye–Hückel radius. The much higher viscosities of the NaA terpolymers may also be explained by the thickness of the Debye ionic layer. The NaAMB and NaAMPS mers are farther from the polymer backbone and may interfere with hydrophobic association more than the NaA mer. Additionally, the *gem*-dimethyl groups of the NaAMB and NaAMPS may have sufficient hydrophobic character to disrupt associations of the *n*-decyl groups into stable micelle-like domains (Figure 8).

Conclusions

Associative polymers of acrylamide and *n*-decylacrylamide with sodium 3-acrylamido-3-methylbutanoate, sodium acrylate, or sodium 2-acrylamido-2-methylpropanesulfonate have been prepared by a micellar technique. The NaAMPS terpolymers display typical polyelectrolyte behavior at low solution ionic strength and high charge density. The sulfonate groups are not sufficiently shielded by the Na counterions to prevent electrostatic repulsions and hydrophobic aggregation at charge densities of 25 mol %. The NaAMB and NaA terpolymers exhibit associative properties at lower ionic strengths and higher charge densities due to hydrophobic associations among the decyl

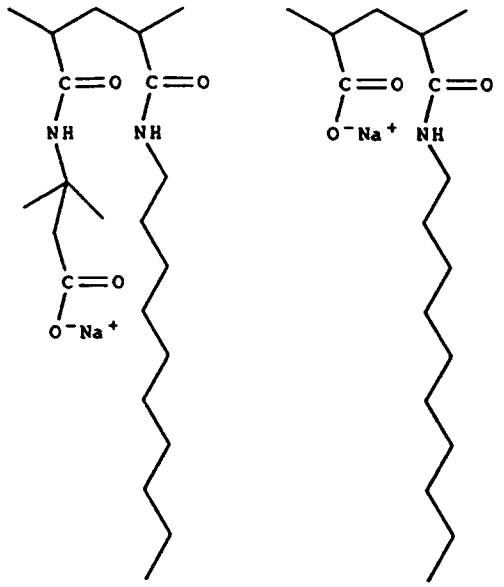

Figure 8. Schematic comparison of NaAMB terpolymer versus NaA terpolymer illustrates how hydrophobic associations might be disrupted by the more extended NaAMB ionic group resulting in less aggregation and lower viscosity.

groups along the polymer chain as the Debye–Hückel reciprocal shielding length (κ^{-1}) is reduced to the order of the decay length for long-range hydrophobic interactions.

Distance of the ionic group from the backbone seems to influence hydrophobic association also. The NaAMB and NaAMPS monomers allow charged groups to extend out farther from the polymer backbone, apparently preventing associations among the hydrophobic decyl groups at low solution ionic strengths and high polymer charge density. This is not observed for the NaA monomer with charge much closer to the backbone. As the polymer coils interact, a critical apparent molecular weight is reached and viscosity exponentially increases with increasing polymer concentration.

Although the goals of achieving facile dissolution of associative viscosifiers and understanding more fully the effects of ionic monomer composition on solution behavior have been realized, a number of significant problems remain unresolved. First, the precise composition of these *n*-alkyl type terpolymers is not determinable by current methods of analysis. Second, although preliminary data have been presented and discussed at major symposia,[17,18] the precise nature of micellar polymerization has not been elucidated, in particular sequence length of hydrophobic monomers produced by the method and its importance on macroscopic viscosity. Finally, molecular weight data for associative polymers, particularly those with blocky microstructures, are suspect since intermolecular associations during dissolution may not be completely disrupted. Therefore, comparisons can only be made (and then cautiously) on systems prepared under similar synthetic conditions. Each of these concerns will be addressed in subsequent papers in this series.[36,37]

Acknowledgment. Financial support for this work provided by the Department of Energy, the Office of Naval Research, and the Defense Advanced Research Projects Agency is gratefully acknowledged.

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Registry No. AM/C10AM/NaAMB (copolymer), 126509-34-0; AM/C10AM/NaA (copolymer), 126461-18-5; AM/C10AM/NaAMPS (copolymer), 114859-64-2; NaCl, 7647-14-5.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1992	Journal article

4. TITLE AND SUBTITLE
Apparent Solubility Parameters from Photophysical Investigation of Copolymers with Pendent Naphthyl Chromophores

5. FUNDING NUMBERS
C: N00014-89-J-1893

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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8. PERFORMING ORGANIZATION REPORT NUMBER
91-92-3

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Avenue
Arlington, VA 22217

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Published in Polymer International, 1992, 27(1), 63-65

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)
See attachment

14. SUBJECT TERMS

15. NUMBER OF PAGES
3

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Unlimited

Polymer International 27 (1992) 63–65

Apparent Solubility Parameters from Photophysical Investigation of Copolymers with Pendent Naphthyl Chromophores

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(Received 25 October 1990; revised version received 5 April 1991; accepted 13 May 1991)

Abstract: The effect of solvent on the formation of excimer from copolymers of 2-(1-naphthylacetyl)ethylacrylate (NAEA) with both acrylamide (AM) and *N*-vinyl pyrollidone (VP) in dilute solution was investigated. A minimum in excimer intensity was observed for each of the copolymers at approximately $2{\cdot}20 \times 10^4$ $(J/m^3)^{0{\cdot}5}$. It is suggested that the relatively high content of NAEA in the copolymers (between 30 and 60%) governs the overall solubility parameter of the polymer.

Key words: naphthalene-containing copolymers, photophysical studies, solubility parameter, excimer.

INTRODUCTION

Excimer formation in polymers containing covalently bound chromophores has been used extensively to study polymer structure and mobility in solutions.[1,2] In dilute solutions, the distinguishing feature of polymer excimers is that they are independent of concentration and are therefore totally intramolecular in nature. For isolated polymer coils, excimer intensity is directly related to conformational constraints in a particular solvent system. In a good solvent, for example, excimer formation is largely due to interactions between adjacent chromophores. In a poor solvent, the tighter coiling of the polymer chain causes non-adjacent chromophores to come into close contact with one another, thus facilitating an increase in excimer formation (Fig. 1). In 1969, Nishihara & Kaneko found a linear relationship between excimer intensity (expressed as the excimer to monomer intensity ratio, I_E/I_M) and the intrinsic viscosity for polystyrene.[3] Excimer fluorescence has also been used to determine the Hildebrand solubility parameter of pyrene-labelled polystyrene copolymers of different molecular weights.[4] In this work the authors have employed such techniques to determine the apparent solubility parameters $(J/m^3)^{0{\cdot}5}$ of copolymers containing 30–60 mol% of pendent naphthalene chromophore units.

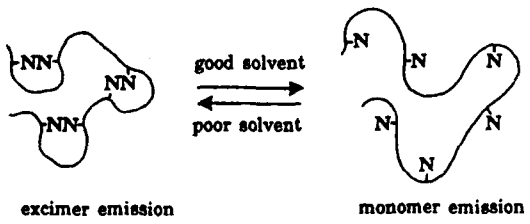

Fig. 1. Schematic of solvent effect on excimer formation in dilute polymer solutions.

EXPERIMENTAL

The synthesis and characterization of both 2-(1-naphthylacetyl)ethylacrylate (NAEA) and its copolymers with acrylamide (30·3 and 48·6 mol% NAEA) and vinyl pyrollidone (59·6 mol% NAEA) have been reported previously.[5] All solvents (Table 1) were spectroscopic grade and were used without further purification. Hildebrand solubility parameters $(J/m^3)^{0{\cdot}5}$ for these solvents were obtained from the literature.[6] Molecular weights of the polymers, as determined by membrane

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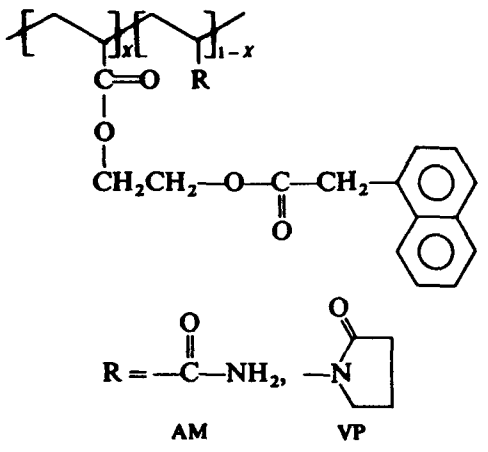

NAEA copolymers

osmometry, were found to be approximately $6{\cdot}0 \times 10^4$. The polymer solutions were prepared as follows. Approximately 1 mg of polymer was added to a vial containing 20 ml of solvent and was stirred at room temperature for 24 h. Each solution was filtered using a Teflon filter. No indication of polymer fractionation or incomplete dissolution was evident. As determined from UV measurements, the concentration of polymer was such that the concentration of chromophore in the solution was $< 10^{-4}$ mol/litre. Samples were purged with nitrogen for at least 10 min prior to emission measurements, and all measurements were made at 25°C. The wavelength of excitation was 280 nm. Monomer and excimer intensities were measured at 330 and 400 nm, respectively, using a Perkin–Elmer 650-10S spectrophotometer.

TABLE 1. Hildebrand solubility parameters for the solvents used in this study

Solvent	δ $(J/m^3)^{0.5} \times 10^{-3}$
Ethanol	26·0
Dimethylformamide	24·8
Dimethylsulfoxide	24·6
Dimethylacetamide	22·1
Ethylene chloride	20·1
Methylene chloride	19·8
Chlorobenzene	19·4
Benzene	18·8
p-Xylene	18·0

RESULTS AND DISCUSSION

The reactivity ratios for both the NAEA–AM and the NAEA–VP comonomer pairs (Table 2) were determined from copolymer compositional data (UV absorbance and elemental analysis). These ratios, which may be employed to determine microstructural characteristics of copolymers, suggest that NAEA–AM copolymers and NAEA–VP copolymers possess distinctly different microstructures. That is, the product of the reactivity ratios ($r_1 r_2$) indicates that the AM copolymers are almost totally random ($r_1 r_2 = 1$) while the VP copolymer displays a high tendency toward alternation ($r_1 r_2 \ll 1$).

Studies of I_E/I_M for these polymers in several different solvents demonstrate a somewhat expected dependence on the nature or solubility parameter (δ) of the solvent

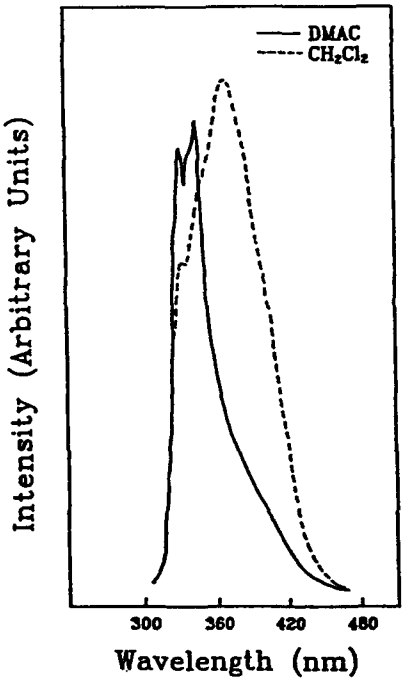

Fig. 2. Steady state fluorescence spectra of NAEA(59·6)–VP in dimethylacetamide (DMAC) and methylene chloride (CH_2Cl_2).

TABLE 2. Reactivity ratios for copolymerization of NAEA

Copolymerization conditions and r_1–r_2 calculation method	r_1	r_2	$r_1 r_2$	Correlation coefficient
NAEA(M_1)–AM(M_2) (DMF, 65°C, AIBN)				
Fineman–Ross method	1·00	0·86	0·86	0·983
Kelen–Tudos method	1·10	0·93	1·02	0·982
NAEA(M_1)–VP(M_2) (DMF, 65°C, AIBN)				
Fineman–Ross method	0·43	0·02	0·01	0·997
Kelen–Tudos method	0·44	0·02	0·01	0·995

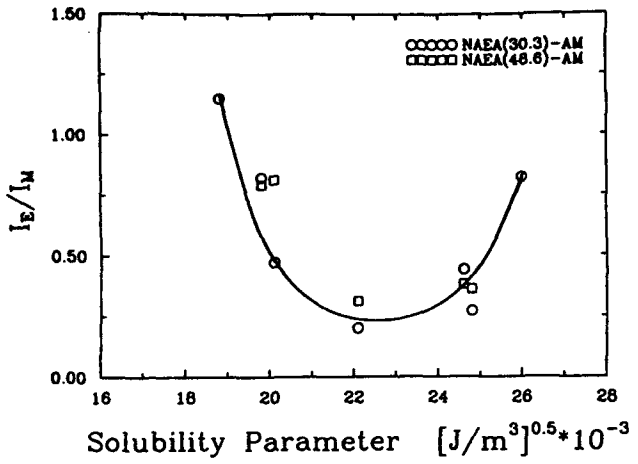

Fig. 3. Effect of solvent solubility parameter on excimer/monomer ratio for NAEA–AM copolymers.

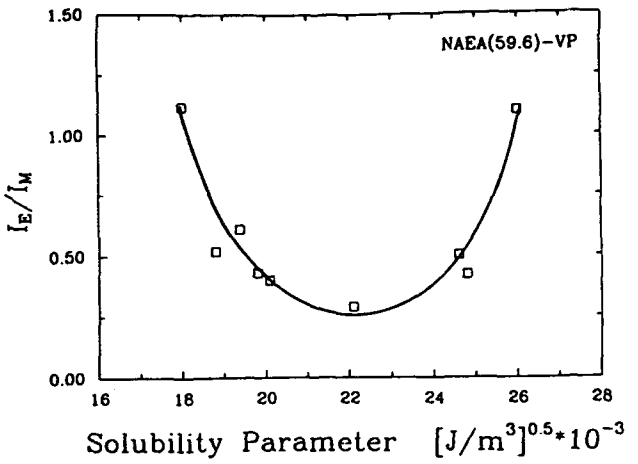

Fig. 4. Effect of solvent solubility parameters on excimer/monomer ratio for NAEA–VP copolymer.

(Fig. 2); however, the apparently similar solution behavior that is observed for the three different copolymer systems is quite surprising. As the solubility parameter of the solvent is increased, a minimum in excimer intensity is observed at δ of approximately $2{\cdot}20 \times 10^4$ $(J/m^3)^{0{\cdot}5}$ for both the AM copolymers (Fig. 3) and the VP copolymer (Fig. 4).

From these results, it may be concluded that each of these three copolymers has an apparent solubility parameter of $2{\cdot}20 \times 10^4$ $(J/m^3)^{0{\cdot}5}$. It is important to consider the fact that all three copolymers contain a relatively high concentration (30–60%) of the NAEA monomer. One explanation for the apparent similarities of the three polymers is that the naphthalene moiety, which has a solubility parameter of $2{\cdot}03 \times 10^4$ $(J/m^3)^{0{\cdot}5}$, is primarily responsible for the observed solubility characteristics.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the United States Department of Energy, Office of Naval Research and the Defense Advanced Research Projects Agency for partial funding of this research.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1992	Journal article

4. TITLE AND SUBTITLE
Water-Soluble Copolymers. 39. Synthesis and Solution Properties of Associative Acrylamido Copolymers with Pyrenesulfonamide Fluorescence Labels

5. FUNDING NUMBERS
C: N00014-89-J-1893

6. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NUMBER
91-92-4

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Avenue
Arlington, VA 22217

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Published in Macromolecules, 1992, 25(7), 1881-1886

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)
See attachment

14. SUBJECT TERMS

15. NUMBER OF PAGES
6

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Unlimited

Water-Soluble Copolymers. 39. Synthesis and Solution Properties of Associative Acrylamido Copolymers with Pyrenesulfonamide Fluorescence Labels

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Received August 16, 1991; Revised Manuscript Received December 10, 1991

ABSTRACT: Pyrenesulfonamide-labeled model associative polymers have been prepared via copolymerization of acrylamide with 0.5 mol % *N*-[(1-pyrenylsulfonamido)ethyl]acrylamide. Synthesis of this monomer and details of copolymerization with acrylamide via surfactant and solution copolymerization techniques are described. The microheterogeneous surfactant technique yields a copolymer which exhibits intermolecular associative behavior in aqueous media as demonstrated by rheological and steady-state fluorescence studies. Conversely, classical light scattering studies indicate the compact nature of the copolymer prepared by the homogeneous solution technique. Intramolecular hydrophobic associations, indicated by a low second virial coefficient and a small hydrodynamic volume, dominate rheological behavior.

Introduction

Microheterogeneous phase separation in hydrophobically-modified water-soluble copolymers can be achieved by appropriate structural tailoring, yielding systems with unique rheological characteristics. Among such materials are rheology modifiers known as "associative thickeners" which demonstrate significant increases in viscosity above the critical overlap concentration, C^*.[1] For example, the copolymer of acrylamide containing 0.75 mol % *n*-decylacrylamide prepared under suitable conditions[2] exhibits a 16-fold increase in apparent viscosity (Figure 1) as the copolymer concentration increases from 0.05 to 0.20 g/dL. Homopolyacrylamide, by comparison, prepared under the same reaction conditions shows only a gradual increase in viscosity with concentration.

Although associative thickeners based on hydrophobic modification of a number of polymer types including polyacrylamides, cellulosics, polyethers, etc., have been reported, the mechanisms responsible for their rheological behavior have yet to be fully elucidated. The low concentration of "hydrophobes" and the nature of the interactions preclude study by traditional spectroscopic techniques such as IR or NMR due to insufficient resolution. Photophysical techniques with appropriately labeled copolymers, however, have been used by our group and others[3,4] to study such systems.

In this paper we report synthesis and solution properties of copolymers of acrylamide with *N*-[(1-pyrenylsulfonamido)ethyl]acrylamide. The pyrenesulfonamide comonomer serves in two capacities in this study; it provides a fluorescence label for photophysical measurements, and it serves as the hydrophobic monomer. Under selected reaction conditions discussed herein associative properties are observed. The subsequent paper in this series details photophysical evidence for the associations.

Experimental Section

Materials. Acrylamide (AM) was recrystallized from acetone three times and vacuum-dried at room temperature prior to use. Pyrene was purified by flash chromatography[5] (silica gel packing; CH_2Cl_2 eluent). *N,N*-Dimethylformamide (DMF) was allowed to stand overnight over 4-Å molecular sieves and was then distilled at reduced pressure. H_2O was deionized and had a conductance of less than 1×10^{-7} mho/cm. Other starting materials were purchased commerically and used as received. Solvents were reagent-grade, unless otherwise noted.

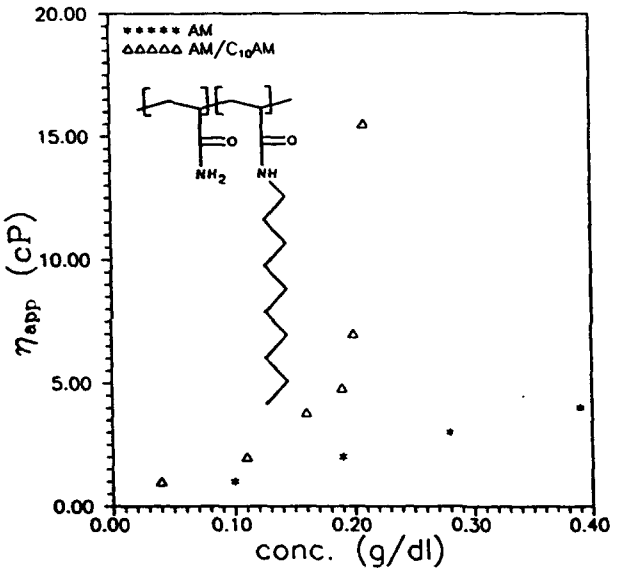

Figure 1. Illustration of associative behavior of polyacrylamide modified with 0.75 mol % *n*-decylacrylamide via surfactant polymerization.

Monomer and Model Compound Synthesis. *N*-[(1-Pyrenylsulfonamido)ethyl]acrylamide (5) and Its Precursors (Schemes I and II). Sodium 1-Pyrenesulfonate (7). A literature method[6] was modified for the preparation of sodium 1-pyrenesulfonate. Pyrene (6; 47.60 g, 0.235 mol) was dissolved in 300 mL of CH_2Cl_2. Chlorosulfonic acid (16 mL, 0.24 mol) dissolved in 50 mL of CH_2Cl_2 was added dropwise to the pyrene solution with brisk stirring, at 0 °C, under a steady nitrogen stream. The reaction progress was followed by TLC (CH_3OH eluent); 1-pyrenesulfonic acid appears at $R_f = 0$ while pyrene has a higher R_f value. The resulting dark-green solution was poured (with extreme caution) into 500 cm³ of ice and stirred, allowing the CH_2Cl_2 to evaporate over a 2-day period. This solution was filtered twice through Celite to remove particulates; each time the Celite pads were washed with 1 × 150 mL of H_2O. NaOH (10.0 g, 0.25 mol) was added as an aqueous solution. Aqueous NaCl (500 cm³) was also added. The yellow sodium salt 7 was precipitated via slow solvent evaporation, filtered, and vacuum-dried at 65 °C. Elemental analysis indicated that this product was a dihydrate and contained residual NaOH. This salt was used successfully in the subsequent reaction without further

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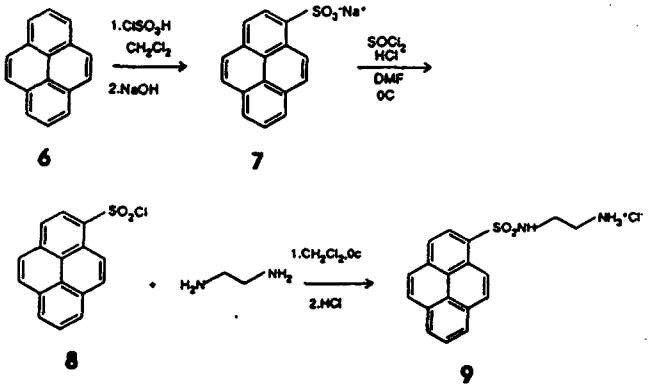
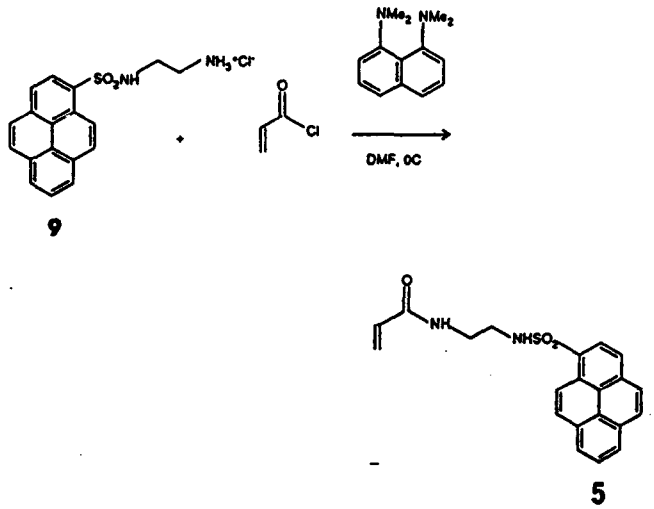
Scheme I
Synthesis of *N*-(1-Pyrenylsulfonyl)ethylenediamine Hydrochloride (9)



Scheme II
Synthesis of *N*-[(1-Pyrenylsulfonamido)ethyl]acrylamide (5)



purification. Yield: 51.0 g (71%). Anal. Calcd for $C_{16}H_{13}O_5SNa$: C, 56.46; H, 3.85; S, 9.42; Na, 6.76. Found: C, 55.64; H, 3.15; S, 9.33; Na, 8.71. IR: 3100–3700 (OH stretch due to H_2O); 3045 (aromatic CH stretch); 1194 and 1060 (asymmetric and symmetric S=O stretch) cm^{-1}. ^{13}C NMR (DMSO-d_6): δ 123.72, 124.82, 125.34, 126.26, 126.74, 126.80, 126.88, 127.29, 127.69, 130.11, 130.71, 131.29, 141.81 (all aromatic resonances).

1-Pyrenesulfonyl Chloride (8). A hydrochloric acid solution in diethyl ether (30 mL, 3×10^{-2} mol) was added to a slurry of 7 (9.1 g, 3×10^{-1} mol) in DMF (200 mL) to generate the sulfonic acid. Thionyl chloride (22 mL, 0.18 mol) was then added dropwise. TLC with 3:1 CH_2Cl_2/acetone eluent showed the disappearance of the starting material ($R_f = 0$) and the appearance of 8 ($R_f = 0.6$). Stirring was continued for 3 h, and then the solution was poured into 400 cm^3 of ice. The orange-yellow precipitate was filtered and washed with 500 mL of H_2O. This material was air-dried overnight on the filter and then vacuum-dried for 18 h at 100 °C. Yield: 7.7 g (85%). Mp: 172 °C. Anal. Calcd for $C_{16}H_9SO_2Cl$: C, 63.89; H, 3.00; S, 10.67; Cl, 11.78. Found: C, 63.85; H, 3.09; S, 10.61; Cl, 11.59. IR: 3107, 3145 (aromatic CH stretch); 1590 (SCl stretch); 1361, 1173 (asymmetric and symmetric S=O) cm^{-1}. ^{13}C NMR (DMSO-d_6): δ 123.79, 123.9[illegible] 124.34, 124.93, 125.52, 126.40, 126.73, 126.99, 127.36, 127.91, 130.19, 130.78, 131.52, 141.55 (all aromatic resonances).

***N*-(1-Pyrenylsulfonyl)ethylenediamine Hydrochloride (9).** A modification of a literature procedure for the reaction of acid chlorides with symmetrical diamines,[7] via a high-dilution technique, was used for the synthesis of 9. Ethylenediamine (10.0 mL, 0.15 mol) was added to 1 L of CH_2Cl_2 and stirred rapidly at 0 °C under a nitrogen blanket. 8 (3.0 g, 1.0×10^{-2} mol) was dissolved in 1 L of CH_2Cl_2 and added dropwise to the stirred diamine solution. After addition was completed (about 2 h), the CH_2Cl_2 layer was extracted with 2 × 3 L of H_2O and 1 × 2 L of 5% NaCl. The CH_2Cl_2 layer was slowly filtered through a pad of $MgSO_4$ and then treated with 15 mL of 1.0 N HCl dissolved in diethyl ether. The resulting fine pale-yellow precipitate was vacuum-dried at room temperature. TLC of this material (3:1 CH_2Cl_2/acetone eluent) exhibited only one component at R_f = 0. HPLC purity was determined to be >99.9%. Anal. Calcd for $C_{18}H_{17}SO_2N_2Cl$: C, 59.92; H, 4.72; N, 7.77; S, 8.89; Cl, 9.83. Found: C, 59.92; H, 4.59; N, 7.57; S, 8.64; Cl, 9.81. IR: 2800–3600 (NH_3-Cl stretch); 3318 (*HN*SO_2 stretch); 3028 (aromatic CH stretch); 2912 (aliphatic CH stretch); 1325, 1159 (asymmetric and symmetric S=O); 1085 (SN stretch) cm^{-1}. ^{13}C NMR (DMSO-d_6): δ 38.61, 39.87 (ethylene resonances); 123.06, 123.28, 124.15, 126.77, 126.96, 129.63, 129.96, 130.40, 131.60, 134.05 (aromatic resonances).

The free amine of 9 was prepared via addition of a concentrated aqueous solution of a molar equivalent of NaOH to 9 dissolved in the minimum amount of DMF. After brief stirring, the solution was poured into H_2O, which precipitated 9 in the free amine form, designated here as 10. This yellow solid was washed with H_2O and then vacuum-dried at room temperature. A downfield shift of the ethylene resonances was observed in the ^{13}C NMR spectrum, confirming the formation of the free amine.[8] ^{13}C NMR (DMSO-d_6): δ 42.62, 46.03 (ethylene resonances); 123.20, 123.46, 124.17, 126.77, 126.96, 129.70, 129.87, 130.53, 131.60, 134.05 (aromatic resonances).

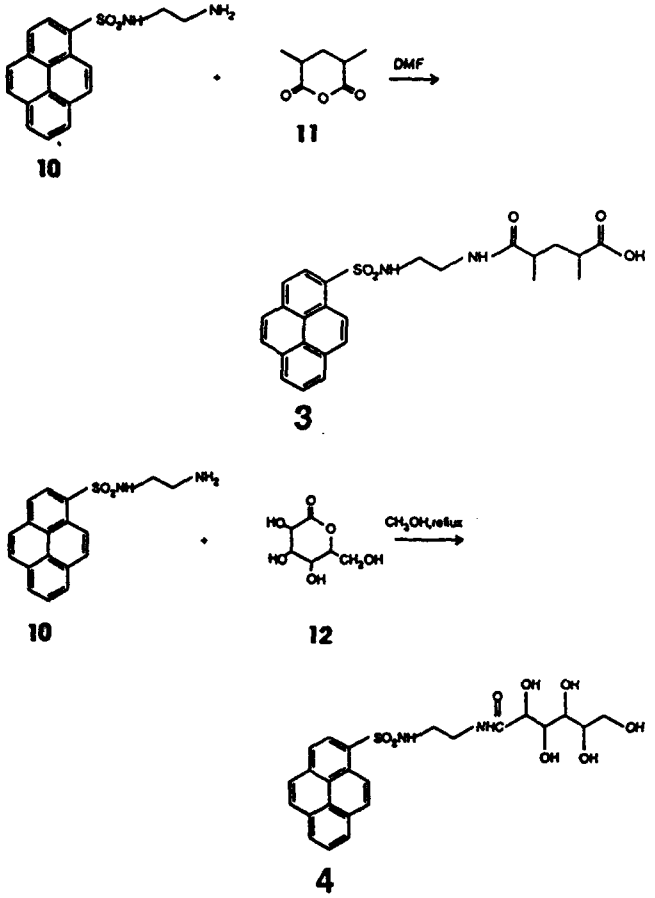
***N*-[(1-Pyrenylsulfonamido)ethyl]acrylamide (5).** The synthesis of 5 is depicted in Scheme II. The amine hydrochloride salt 9 (1.0 g, 2.8×10^{-3} mol) and 1,8-bis(dimethylamino)naphthalene (1.19 g, 5.6×10^{-3} mol) were stirred with 7 mL of DMF under a nitrogen stream for 15 min at 0 °C. Acryloyl chloride (2.2 mL, 2.8×10^{-2} mol) in 7 mL of DMF was then added dropwise to the amine solution. TLC (acetone eluent) was used to follow the depletion of the starting amine (R_f = 0) and the generation of the product (R_f = 0.70). After the addition was complete, the reaction mixture was poured into 150 cm^3 of ice. The product precipitated overnight as a yellow solid, which was subsequently filtered and vacuum-dried at room temperature. Yield: 0.90 g (88%). Product recrystallization was performed by dissolution of 0.9 g of 5 in 300 mL of boiling CH_2Cl_2, decolorization with Norit RB 1 0.6 charcoal pellets, and filtration through a Celite pad. Pale-green crystals formed, which were recovered in 69% yield. Purity of this material was determined to be >99.9% via HPLC. Anal. Calcd for $C_{21}H_{18}SO_3N_2$: C, 66.67; H, 4.76; S, 8.47; N, 7.41. Found: C, 66.83; H, 5.00; S, 8.48; N, 7.49. IR: 3050–3600 (NH stretch); 3370, 3289 (*HN*SO_2 stretch); 3084 (aromatic CH stretch); 2938, 2864 (aliphatic CH stretch); 1659, 1540 (amide I and II bands); 1312, 1159 (S=O asymmetric and symmetric stretch) cm^{-1}. ^{13}C NMR (DMSO-d_6): δ 38.77, 41.95 (ethylene carbons); 127.14, 129.58 (vinylic carbons); 123.09, 123.32, 124.07, 124.27, 125.02, 126.63, 126.79, 126.86, 129.44, 129.73, 130.36, 131.44, 132.23, 133.88 (aromatic carbons); 164.84 (acrylamido ketone carbon).

Pyrenesulfonamide Model Compounds. 2,4-Dimethyl-*N*-[(1-pyrenylsulfonamido)ethyl]glutaramide (3). Synthesis of 3 required first the preparation of 2,4-dimethylglutaric anhydride, followed by amination with 10 (Scheme III).

2,4-Dimethylglutaric Anhydride (11). 2,4-Dimethylglutaric acid (2.0 g) was added to 5 mL of acetic anhydride. Vacuum distillation of this solution at 90 °C gave acetic anhydride as the first fraction. The anhydride product 11 then distilled over as a clear liquid which cooled to form a hygroscopic, hard white solid. Although an IR of this product showed the presence of some diacid (OH stretch 2500–3500 cm^{-1}; C=O stretch due to diacid at 1698 cm^{-1}), this material was successfully used in subsequent reactions without purification. Yield: 1.1 g (62%). IR: 3500–2500 (OH stretch due to acid), 1794, 1752 (asymmetrical and symmetrical anhydride ketone stretching modes); 1698, 1459 (acid ketone stretching modes) cm^{-1}.

Synthesis of 3 (Scheme III). The amine sulfonamide 10 (0.75 g, 2.31×10^{-3} mol) was dissolved in 6 mL of DMF. This solution was added dropwise to 11 (0.41 g, 2.54×10^{-3} mol) dissolved in 2 mL of DMF under N_2 at 0 °C. The reactant mixture was stirred for 5 h and then poured into 50 mL of saturated NaCl solution, which was acidified (HCl). A yellow oil immediately formed. The H_2O was decanted and the product dissolved in 30 mL of CH_2Cl_2. Extraction of this solution with 50 mL of H_2O

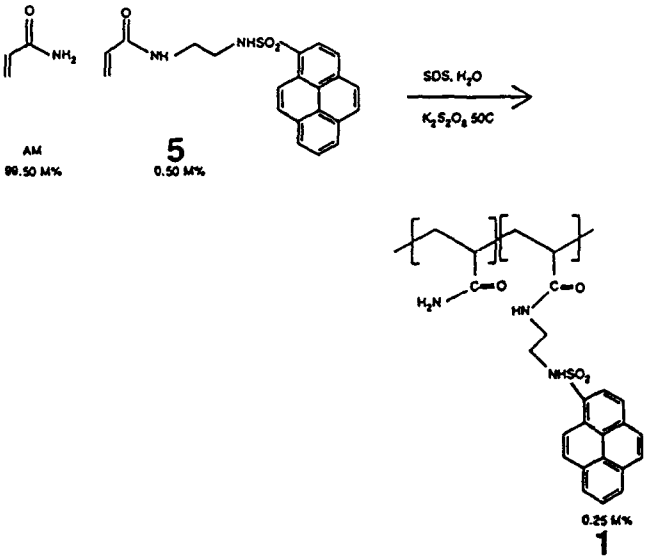
Scheme III
Synthesis of Pyrene-Containing Model Compounds 3 and 4



precipitated the product as a pale-green solid. TLC (CH_3OH eluent) gave a $R_f = 0.82$ for the product; traces of impurities near $R_f = 0$ were also present. Purification of **3** was performed via dissolution of 0.61 g in DMF, followed by flash chromatography on 250 mL of silica gel, with CH_3OH as the eluent. This procedure was tedious since the product was very slow to elute. Vacuum solvent removal from the pure fractions gave about a 0.2-g (33%) yield of a pale-yellow-green product. The HPLC purity of this material was determined to be >99.9%. Anal. Calcd: C, 64.35; H, 5.63; N, 6.01; S, 6.87. Found: C, 64.20; H, 5.69; N, 5.94; S, 6.73. IR: 3500–2500 (acid OH stretch); 3378, 3284 (*HN*SO_2 stretching); 1737 (asymmetric C=O stretch of the acid residue); 1684 (amide I); 1549 (amide II); 1302, 1167 (asymmetric and symmetric S=O stretch). ^{13}C NMR (DMSO-d_6): 20.37, 21.13, 21.56 (aliphatic resonances of the glutaric residue); 42.84, 45.30 (aliphatic resonances of the ethylenediamine residue); 126.94, 127.92, 130.63, 133.23, 135.99, 137.62 (aromatic resonances); 179.01, 180.80 (ketone resonances of the glutaric residue).

***N*-[(1-Pyrenylsulfonamido)ethyl]gluconamide Heptahydrate (4).** Synthesis of **4** is depicted in Scheme III. The free amine of **10** (0.44 g, 1.36×10^{-3} mol) was added to δ-gluconolactone (**12**; 0.30 g, 1.68×10^{-3} mol) in 2 mL of CH_3OH. A clear green solution was obtained upon heating; a reflux was maintained for 18 h. Compound **4** precipitated from solution as a yellow-green solid. After filtration and washing with CH_3OH, **4** was vacuum-dried overnight at room temperature. The HPLC purity of this compound was determined to be 99.9%. Elemental analysis determined **4** to be a heptahydrate. Yield: 0.31 g (45%). Mp: 171–173 °C. Anal. Calcd (heptahydrate): C, 46.67; H, 4.90; N, 4.53; S, 5.19. Found: C, 46.16; H, 4.55; N, 4.24; S, 5.31. IR: 3600–3000 (OH stretch); 3379 (*HN*SO_2 stretch); 1657 (amide I); 1533 (amide II); 1419 (CN stretch); 1307, 1161 (asymmetric and symmetric S=O) cm^{-1}. ^{13}C NMR (DMSO-d_6): δ 38.24, 41.20 (ethylene resonances); 63.27 (1′COH); 69.89, 71.44, 72.25, 73.45 (2′COH); 123.17, 123.35, 124.22, 126.65, 126.81, 127.09, 129.51, 129.68, 129.62, 130.51, 133.93 (aromatic resonances); 172.77 (amide ketone).

Scheme IV
Synthesis of Copolymer 1 via the Surfactant Polymerization Technique



Synthesis of Pyrenesulfonamide-Labeled Polymers. Poly[*N*-[(1-pyrenylsulfonamido)ethyl]acrylamide-*co*-acrylamide] 1. Surfactant Polymerization Technique. The general method of Turner et al. was employed (Scheme IV).[9] Monomer feed ratio in this copolymerization was 99.50 mol % AM to 0.50 mol % **5**. The polymerization was performed by adding 7.38 g (0.105 mol) of AM, 7.92 g (2.74×10^{-2} mol) of sodium dodecyl sulfate, 0.20 g (5.29×10^{-4} mol) of **5**, and 235 g of H_2O to a 500-mL flask equipped with a mechanical stirrer, nitrogen inlet, condenser, bubbler, and heating bath. This mixture was heated to 50 °C under a nitrogen purge. The stirring rate was maintained at approximately 60 rpm. All of the monomer **5** had dissolved after 15 min; polymerization was then initiated via syringe addition of 9.25×10^{-6} mol of $K_2S_2O_8$ as a deaerated solution in 2 mL of H_2O. Polymerization was allowed to continue at 50 °C for 12 h, after which time the polymer was recovered via precipitation into acetone. Purification was accomplished by redissolving the polymer in H_2O and dialyzing against H_2O using 12 000–14 000 molecular weight cutoff dialysis tubing. The polymer was recovered by freeze-drying. Conversion was 22%.

Poly[*N*-[(1-pyrenylsulfonamido)ethyl]acrylamide-*co*-acrylamide] 2. Solution Polymerization Technique. Monomer feed ratios, quantities, and equipment in this preparation (Scheme V) were the same as in the previous procedure. Comonomers were dissolved in a mixture of 130 mL of DMF and 100 mL of H_2O. Three freeze–pump–thaw cycles were performed to remove residual oxygen. The initiation procedure was as described for the surfactant polymerization. In this case, polymer precipitated from the solution as the polymerization continued (12 h). Pouring the suspension into acetone allowed recovery of the polymer product. Purification procedures were as described for the surfactant polymerization. Conversion was 21%. UV analysis determined **2** to contain 0.35 mol % **5** (70% incorporation).

Characterization Methods. Pyrenesulfonamide Derivatives. ^{13}C NMR spectra were recorded with a Bruker AC-300 instrument. Most samples were dissolved in DMSO-d_6; chemical shift assignments are relative to the central DMSO peak (^{13}C, 39.50 ppm). UV–vis spectra were recorded with a Perkin-Elmer Lambda 6 spectrophotometer. A Mattson Model 2020 FTIR was used to obtain infrared spectra.

Sample purities were determined in most cases by both TLC and HPLC. TLC was performed on Merck Kieselgel 60 silica gel plates. Developed plates were generally viewed under 325-nm light for pyrene derivatives. HPLC was performed on a Hewlett-Packard Model 1050 system equipped with a photodiode-array detector. A Waters μ-Bondapak C18 column was employed with methanol as the mobile phase. The sample effluent was typically monitored at 220 and 350 nm. Alternately, multiple wavelengths

Scheme V
Synthesis of Copolymer 2 in DMF/H_2O

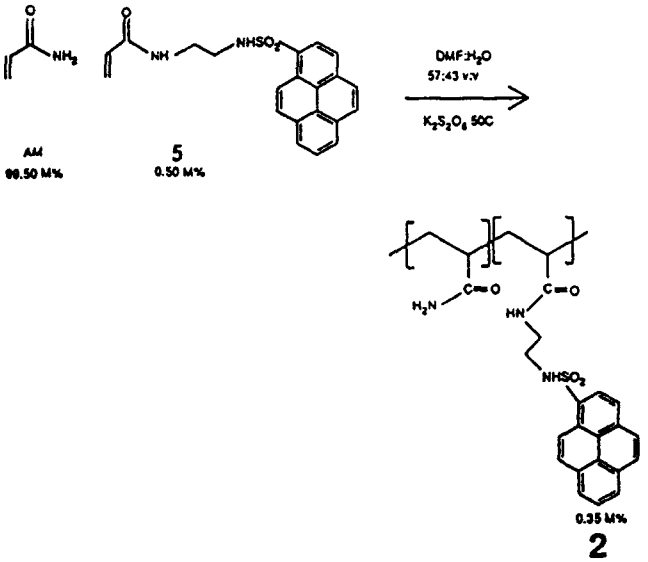


Table I
Stock Solutions of Labeled Polymers

polymer	polym conc, mg/dL	fluorophore conc, mol/L
1	218	7.13×10^{-6}
2	193	9.28×10^{-6}

were monitored—depending on the nature of the suspected impurities.

Solution Preparation. Polymer stock solutions were prepared in H_2O or 2% (w/w) NaCl at ca. 200 mg/dL. Several weeks of constant mechanical shaking were required for complete solubilization. Solutions were filtered through an 8-μm filter; a peristaltic pump was employed to pump the solution at a low flow rate. Polymer and fluorophore concentrations of stock solutions are shown in Table I.

Copolymer Composition. The copolymer composition was determined by UV analysis of the aqueous copolymer solutions. The pyrenesulfonamide chromophore was determined to have $\epsilon = 24120\ M^{-1}\ cm^{-1}$.

Rheological Studies. Viscosity measurements were performed on solutions ranging from 20 to 200 mg/dL in concentration. Measurements were recorded with a Contraves low-shear 30 rheometer at 25 °C and a shear rate of 6.0 s^{-1}.

Classical Light Scattering. Classical light scattering measurements were performed on a Chromatix KMX-6 instrument. A 1.2-μm filter was used in the filter loop. Measurements were made at 25 °C. dn/dc measurements were taken on a Chromatix KMX-16 differential refractometer also at 25 °C.

Results and Discussion

The synthetic objective of this work was to prepare a pyrene-containing monomer which could be copolymerized with acrylamide to yield a copolymer with associative thickening behavior. Our concept was to utilize a hydrolytically stable monomer with both the necessary hydrophobic characteristics and photophysical response. Although fluorescence probes and labels have been used to study organization, we know of no other reports utilizing the fluorescence label as the sole hydrophobic moiety for domain formation.

The monomer *N*-[(1-pyrenylsulfonamido)ethyl]acrylamide (5) proved to have the necessary properties to achieve our synthetic objective. This monomer was initially synthesized and a small quantity provided by Winnik's group.[10] Subsequently we modified synthetic procedures and scaled up the reaction sequence to provide sufficient quantities of purified monomer for polymerization and photophysical investigations.

Several features of 5 should be noted. The acrylamido functionality of the monomer allows rapid copolymerization with the acrylamide monomers. Monomers of this type have large ratios of (k_p^2/k_t) where k_p and k_t represent the rate constants for propagation and termination in free-radical polymerization. The amide and sulfonamide linkages are hydrolytically stable in aqueous media and thus protect the integrity of the label during photophysical analysis. The monomer 5 has no benzylic hydrogens for chain transfer as do most pyrene labels reported in the literature. The spacer length (in this case, ethylene) can be altered in the synthetic procedure to decouple the pyrene from the polymer backbone. Finally the pyrenesulfonamide chromophore has a high molar absorptivity value and a high quantum yield of fluorescence.[11]

The synthesis of 5 deserves some comment. The first synthetic step (Scheme I), chlorosulfonation of pyrene, proceeded smoothly. Product 7, sodium 1-pyrenesulfonate, contained a small amount of NaOH but was used without further purification. The compound was isolated as a dihydrate; similar compounds have been reported to exist as hydrates—for example, 1-pyrenesulfonic acid.[12] Transformation to pyrenesulfonyl chloride (8) was also facile.

The reaction of 8 with ethylenediamine to give *N*-(1-pyrenylsulfonyl)ethylenediamine hydrochloride (9) was problematic. Initial attempts, despite dilute reaction conditions, led to production of significant amounts of the ethylenediamine bis(sulfonamide) which was difficult to separate from 9. Apparently, the reaction is diffusion-controlled. Reaction of 8 with ethylenediamine is quite rapid, and if the desired monosulfonamide product 10 encounters another molecule of 8, the sequential reaction will occur.

Recent literature has addressed control of such reactions. Monoacylation of symmetrical diamines can be achieved by a "high-dilution" technique.[7,13] Therefore, a very dilute solution of 8 was added dropwise to a solution of excess ethylenediamine with rapid mixing to reduce the disubstitution reaction. A pure product was obtained by extraction in methylene chloride and conversion to the amine hydrochloride 9 by addition of HCl in diethyl ether.

Reaction of 9 with acryloyl chloride (Scheme II) was facilitated by using 2 equiv of the acid scavenger 1,8-bis(dimethylamino)naphthalene. This base is sterically hindered[14] and will not deprotonate the sulfonamide proton 5. The sulfonamide proton of 5 is acidic; triethylamine and other bases deprotonate 5 to give the sulfonamide salt, which is nonfluorescent. The pyrenesulfonamide monomer 5 was recrystallized from methylene chloride. HPLC analysis utilizing dual ultraviolet detection at 330 and 220 nm indicated a sample purity greater than 99.9%.

In addition to the desired sample purity, monomer 5 is soluble in aprotic solvents such as dimethylformamide and dimethylacetamide. It is insoluble in water but, importantly, is readily solubilized by sodium dodecyl sulfate micelles.

Model compounds 3 [2,4-dimethyl-*N*-[(1-pyrenylsulfonamido)ethyl]glutaramide] and 4 [*N*-[(1-pyrenylsulfonamido)ethyl]gluconamide heptahydrate] were synthesized as water-soluble species bearing the pyrenesulfonamide moiety for model studies (Scheme III). Neither 3 nor 4 has been previously reported. Structural and purity evaluations of both were satisfactory. Interestingly, despite extended drying, 3 remained a heptahy-

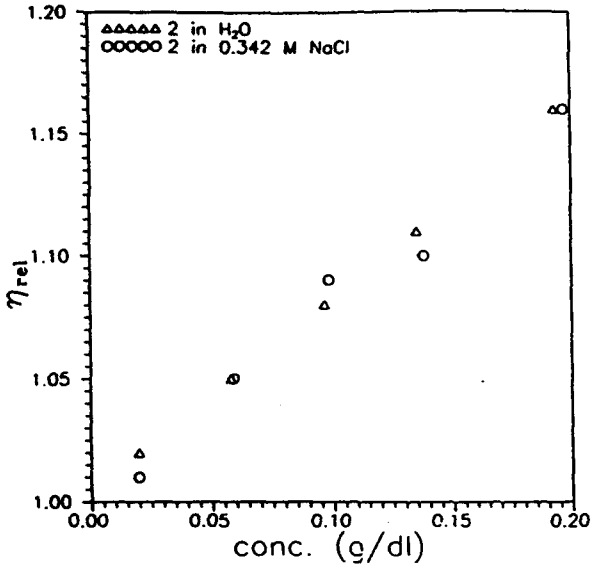


Figure 2. Relative viscosity vs concentration for copolymer 2 in H_2O (Δ) and in NaCl (O).

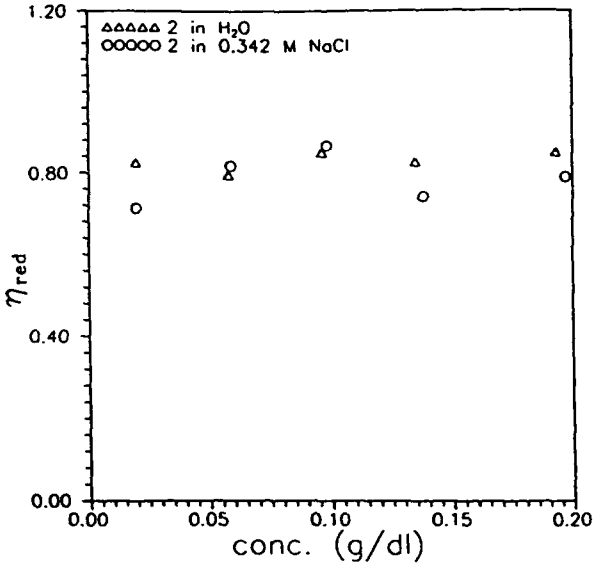


Figure 3. Reduced viscosity vs concentration for copolymer 2 in H_2O (Δ) and in NaCl (O).

drate. Other hydrophobic gluconamides have also been reported to have highly hydrated structures.[15]

Synthesis of Model Polymers. Two synthetic methods were chosen to prepare copolymers with approximately 0.5 mol % 5 but different microstructures. In the first procedure, often called the "micellar technique", 99.5 mol % acrylamide and 0.5 mol % 5 were copolymerized in aqueous solution in the presence of sodium dodecyl sulfate at concentrations well above its critical micelle concentration (Scheme IV). Potassium persulfate was used as the initiator.

Concurrent studies in our laboratories with phenyl and naphthyl chromophore-containing monomers have shown that in this microheterogeneous procedure the surfactant/hydrophobic monomer ratio is important in dictating final rheological properties.[16] These findings are consistent with a proposed mechanism of successive chain propagation of hydrophobic monomers present in the separate SDS micelles and solution polymerization of acrylamide resulting in short runs of the comonomer randomly distributed along the polymer backbone. The importance of this distribution will be addressed later in this report.

In a second synthetic procedure (Scheme V) the two monomers in the same molar ratios were copolymerized under homogeneous reaction conditions in a DMF/H_2O mixture again with potassium persulfate initiation. This polymerization might be expected to occur in a more random fashion than the micellar polymerization with monomers of 5 randomly distributed along the backbone.

Copolymer Characterization. The micellar copolymer 1 was purified by successive precipitation into acetone, redissolution into water, dialysis to remove the surfactant, and freeze drying. Verification of the removal of SDS was obtained using the $BaCl_2$ reagent. Copolymer 2 precipitated as a suspension during polymerization and was purified by sequential addition to acetone, filtration, redissolution into water, and lyophilization.

Copolymer compositions were determined by ultraviolet spectroscopic analysis in water of the pyrenesulfonamide chromophore at 351 nm ($\epsilon = 24\,120\ M^{-1}\ cm^{-1}$). Copolymer 1 was found to contain 0.25 mol % 5 (50% incorporation), while copolymer 2 contained 0.35 mol % (70% incorporation). Fluorescence studies which include characterization of the microstructure of copolymers 1 and 2 are reported in the following paper in this issue.

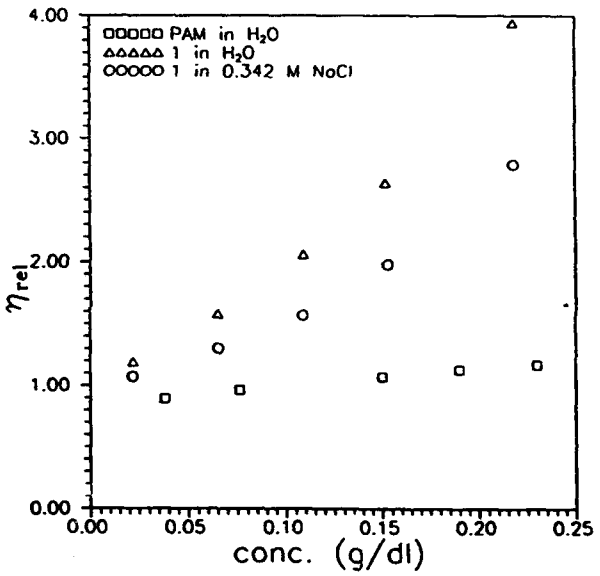


Figure 4. Relative viscosity vs concentration for copolymer 1 in H_2O (Δ) and in NaCl (O) and for homopolyacrylamide in H_2O (□).

Rheological Studies

Rheological studies were performed on diluted stock solutions (Table I). Copolymer 1 prepared by the micellar technique, like many other associative copolymers synthesized previously in our labs, required several weeks with continuous shaking for complete dissolution. A Contraves low-shear 30 rheometer operating at 6 s^{-1} was utilized for viscometric studies.

Equations 1 (the Huggins equation) and 2 (the "modified Einstein–Simha" equation) are often utilized to study polymer solution behavior. The utility of the Huggins

$$\eta_{red} = [\eta] + k'[\eta]^2 C \quad (1)$$

$$\eta_{rel} = 1 + [\eta] C \quad (2)$$

equation (eq 1) is well recognized for solvated polymers; alternately, eq 2 has been proposed for the analysis of polymers which behave as suspensions in solution.[17] Plots of the relative viscosity versus concentration for 2, the solution-polymerized system, are illustrated in Figure 2

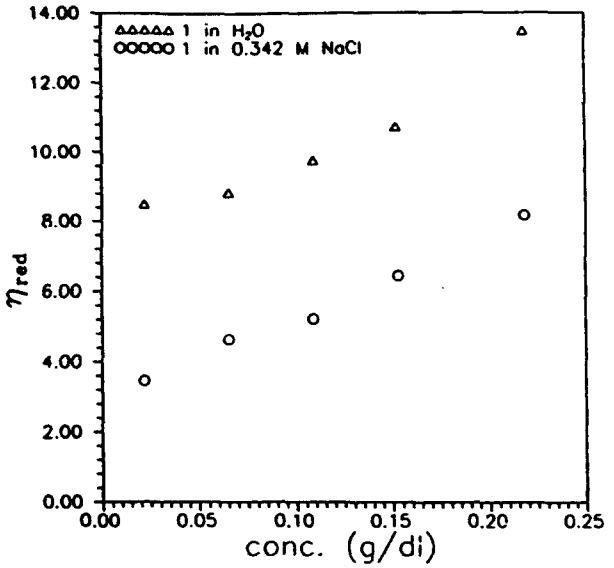


Figure 5. Reduced viscosity vs concentration for copolymer 1 in H_2O (△) and in NaCl (○).

in deionized H_2O and 2% NaCl. The linearity of the data and an intercept value of 1 suggest that this polymer behaves as a suspension in solution. The higher order terms of the Huggins equation, which account for interpolymer interactions, appear to be unimportant here. Huggins plots of these data in water and NaCl are given in Figure 3. The reduced viscosity is insensitive to the polymer concentration (within experimental error), giving a value of zero for the Huggins constant.

These data and fluorescence data to be presented later suggest the presence of intramolecular hydrophobic associations of the pyrenesulfonamide label. Such associations could result in compaction of the polymer coil, giving the observed suspensionlike behavior. Classical light scattering was performed on copolymer 2 in deionized H_2O indicating $M_w = 1.6 \times 10^5$ with $A_2 \approx 0$.

Structure 1 is representative of copolymers of 5 with AM prepared by the micellar polymerization technique. Relative viscosity profiles are illustrated in Figure 4 for deionized water and NaCl solutions. At low concentrations (<0.10 g/dL), intermolecular association is apparent. Increased ionic strength (2% NaCl) contracts the polymer coil, yielding a lower viscosity. The low C^* value likely represents the onset of intermolecular hydrophobic associations of the pyrenesulfonamide moieties. By comparison, a homopolymer of acrylamide exhibits linear viscosity behavior throughout this concentration range. Attempts at Huggins plots for 1 are given in Figure 5. The nonlinearity of the profiles indicates the first two terms of the Huggins equation are insufficient to model these data. Such a nonlinear response is strong evidence for intermolecular associative behavior. It should also be noted that the associative tendencies at copolymer 1 in solution preclude analysis by light scattering.

Conclusions

Our objectives in the synthesis and study of model associative polymers necessitated the synthesis of a fluorophore-containing hydrophobic monomer and model compounds. These materials were purified for polymerization and subsequent photophysical studies. The hydrolytically stable, pyrenesulfonamide-labeled monomers are readily copolymerizable with acrylamide via homogeneous (solution) and heterogeneous (micellar) polymerization techniques. Labeled copolymers prepared by the two procedures have significantly different rheological behaviors. The surfactant-polymerized copolymer 1 in aqueous media exhibits a low critical overlap concentration—typical of associative thickener behavior. Conversely, the solution copolymerization yields copolymer 2, which is more spherical in nature. The Huggins profile of this copolymer in aqueous solutions has zero slope, demonstrating a compact conformation. Light-scattering analysis of this copolymer in H_2O gives a second virial coefficient value of zero. Photophysical analysis of these systems has been conducted and is reported in the next paper in this series.

Acknowledgment. Support for this research by grants from the Office of Naval Research, DARPA, the National Science Foundation EPSCOR program, the Department of Energy, and Unilever, is gratefully acknowledged. We express appreciation to Professor Mitchell Winnik of the University of Toronto and his former student Dr. Robert Borg, now at the University of Malta, for synthesizing and supplying an initial sample of the pyrenesulfonamide monomer for reaction modification, scaleup, and copolymer synthesis.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1992	Journal article

4. TITLE AND SUBTITLE
Water-Soluble Copolymers. 40. Photophysical Studies of the Solution Behavior of Associative Pyrenesulfonamide-Labelled Polyacrylamides

5. FUNDING NUMBERS
C: N00014-89-J-1893

6. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NUMBER
91-92-5

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Avenue
Arlington, VA 22217

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Published in Macromolecules, 1992, 25(7), 1887-1895

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)
See attachment

14. SUBJECT TERMS

15. NUMBER OF PAGES
9

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Unlimited

Water-Soluble Copolymers. 40. Photophysical Studies of the Solution Behavior of Associative Pyrenesulfonamide-Labeled Polyacrylamides

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Received August 14, 1991; Revised Manuscript Received December 10, 1991

ABSTRACT: Photophysical studies were conducted on copolymers of acrylamide containing less than 0.5 mol % *N*-[(1-pyrenylsulfonamido)ethyl]acrylamide in order to relate the aqueous solution behavior to the molecular structure. The copolymer prepared via a surfactant technique was shown to possess some inherent blockiness or short runs of the pyrenesulfonamide label in dilute solution. Intermolecular associations were observed above a critical concentration of polymer. I_e/I_m values from steady-state fluorescence paralleled the rheological response as a function of concentration. The copolymer prepared by solution polymerization showed random incorporation of the pyrenesulfonamide comonomer and no intermolecular association tendency over the concentration range studied. The pyrenesulfonamide labels were shown to form ground-state aggregates within relatively accessible hydrophilic environments in both polymers. Associative thickening behavior observed in the surfactant-polymerized copolymer is consistent with microphase organization of hydrophobic pyrenesulfonamide aggregates above a critical concentration. Fluorescence quenching has been used to probe the microenvironment around the label.

Introduction

The polymer solution behavior of polyelectrolytes has previously been elucidated via photophysical studies of pyrene-labeled water-soluble polymers including polyelectrolytes,[1-6] poly(ethylene oxide),[6] (hydroxypropyl)cellulose,[7-11] and poly(*N*-isopropylacrylamide).[12,36,37] Particularly relevant work includes that of Winnik et al.,[7-10] who studied pyrene-labeled (hydroxypropyl)celluloses which serve as model associative thickeners. Photophysical analysis demonstrated the aggregation of neutral hydrophobic polymers in aqueous media[7-10] and the interaction with surfactants[10,11] at the molecular level. Frank et al.,[6] investigating pyrene-end-labeled poly(ethylene glycol) (PEG) in aqueous media, showed the associative behavior at the molecular level via the photophysical response of the pyrene label. Molecular aspects of poly(ethylene glycol)/poly(methyl methacrylate) polymer complexation have also been reported.[13-15]

In this study, we have employed photophysical techniques and model compounds to analyze the molecular solution behavior of previously reported pyrenesulfonamide-labeled polyacrylamides which display associative behavior in aqueous media[35] (Chart I). Copolymer 1 was synthesized by a surfactant or "micellar" technique and copolymer 2 in homogeneous solution using a cosolvent. Our goal is to correlate molecular solution behavior with macroscopic solution viscosity response in order to develop overall structure–property relationships for associative water-soluble polymers.

Experimental Section

Materials. Deionized water used in these studies had a conductance of less than 1×10^{-7} mho/cm. Cetylpyridinium chloride was recrystallized from methanol/diethyl ether. Nitromethane was distilled at atmospheric pressure. Other starting materials were purchased commercially and used as received.

Labeled Polymers and Model Compounds (Chart I). The syntheses of pyrenesulfonamide-labeled copolymers 1 and 2 and model compounds 3 and 4 are described in the previous paper in this issue.[35] Labeled copolymer 1 was prepared via a surfactant copolymerization technique and contains 0.25 mol % pyrenesulfonamide label. Copolymer 2 was synthesized via a solution copolymerization technique and contains 0.35 mol % pyrenesulfonamide label.

Synthesis of the Fluorescence Quencher *N*-Methylpyridinium Chloride. The method of Nakaro et al.[16] was modified. The basic procedure involves synthesis of *N*-methylpyridinium iodide with subsequent ion exchange to give *N*-methylpyridinium chloride.

***N*-Methylpyridinium Iodide.** Anhydrous pyridine (26 mL, 25 g, 0.32 mol), was added to diethyl ether (250 mL). Methyl iodide (39 mL, 0.63 mol) in diethyl ether (50 mL) was added dropwise with stirring to the pyridine solution. After the addition was completed, the addition funnel was replaced with a condenser. Refluxing overnight resulted in a white solid precipitate. *N*-Methylpyridinium iodide is very hygroscopic; therefore, purification was accomplished by washing with multiple portions of diethyl ether under N_2. The ether washings were removed via a filter stick,[17] which allowed a continuous inert atmosphere to be maintained. Vacuum drying at room temperature overnight gave a white solid, yield 53 g (76%).

***N*-Methylpyridinium Chloride.** *N*-Methylpyridinium iodide (39 g, 0.16 mol) and silver chloride (35 g, 0.26 mol) were added to water (50 mL). This suspension was allowed to stir overnight in the dark under a nitrogen blanket. Filtration removed the lime-green silver iodide; the filter cake was washed with additional water (25 mL). To ensure completeness of exchange, the aqueous solution was then passed through a column containing Bio-Rad AG 1-X8 ion-exchange resin (10 cm^3, quaternary ammonium type, chloride form). The aqueous effluent tested negative for iodide (persulfate test) and positive for chloride (silver nitrate test). Freeze-drying of the aqueous solution produced a syrup, which was further dehydrated via azeotropic distillation with toluene. The resulting off-white solid mass was extremely hygroscopic; a nitrogen atmosphere was consistently maintained during all manipulations. Residual toluene was removed via a filter stick. Recrystallization from the minimum amount of boiling anhydrous 1-propanol gave *N*-methylpyridinium chloride as white crystals, which were washed with diethyl ether and vacuum-dried at room temperature. All weighings and transfers of this material as a solid were performed under dry nitrogen; storage was over phosphorus pentoxide. Elemental analysis of this compound indicated that 8.15% H_2O was retained. Recovery: 18 g (88%).

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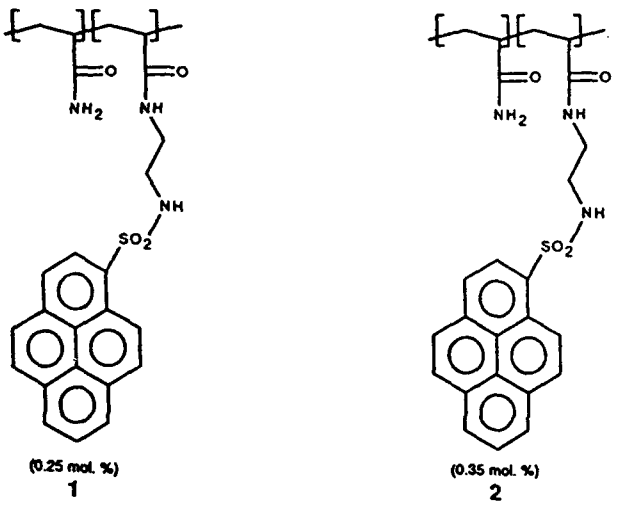
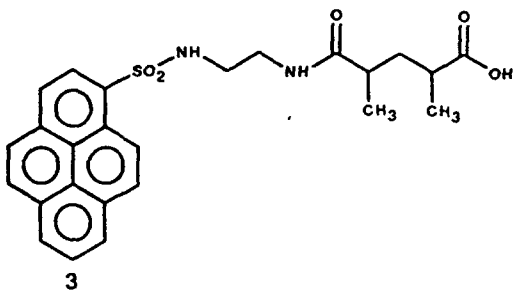
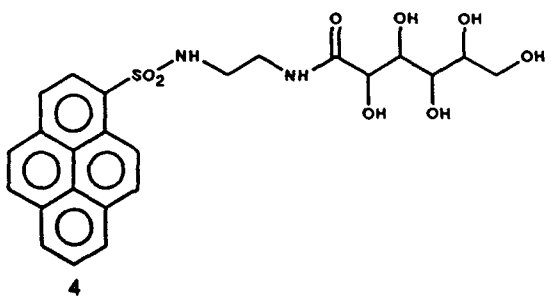
0024-9297/92/2225-1887$03.00/0

Chart I
Pyrenesulfonamide-Labeled Polymers and Model Compounds of This Study







Mp: 138–140 °C (sealed tube). Anal. Calcd: C, 50.87; H, 6.99; Cl, 25.03; N, 9.88. Found: C, 50.58; H, 6.77; Cl, 24.66; N, 9.84. ^{13}C NMR (D_2O, TMS insert): δ 48.25 (CH_3); 128.04, 145.07, 145.30 (aromatic resonances). ^1H NMR (D_2O, TMS insert): δ 3.68 (CH_3); 7.33, 7.80, 8.07 (aromatic CH).

Polymer Characterization. General Procedures. Solution Preparation. Polymer stock solutions were prepared in water or 2% (w/w) aqueous sodium chloride at ca. 200 mg/dL. Several weeks of constant mechanical shaking were required for complete solubilization. Stock solutions were filtered through an 8-μm filter; a peristaltic pump was employed to pump the solution at a low flow rate. Dilution of stock solutions was performed gravimetrically. Samples were allowed to equilibrate for a minimum of 1 week with constant mechanical shaking before characterization.

Characterization. Characterization techniques (other than photophysical) are described in the previous paper in this issue.[35]

Pyrenesulfonamide-Labeled Polymers and Model Compounds. Photophysical Characterization. Steady-State Fluorescence Studies. Steady-state emission studies were performed on a Spex Fluorolog-2 fluorescence spectrometer equipped with a DM3000F data system. All samples were run in the front-face mode to avoid inner filter effects. Slit widths were varied from 0.5 to 2.5 nm, depending on sample concentration. Samples were deaerated by bubbling with nitrogen for 25–30 min. Particularly "foamy" samples were sparged by first bubbling with helium and then with argon. Excitation spectra were obtained via excitation from 250 to 400 nm while monitoring the emission intensity at either 418 nm (monomer emission) or 510 nm (excimer emission). Wavelength-dependent variations in lamp intensity were corrected by an instrumental correction function; Rhodamine B was the internal reference. Detector and emission grating variations were also corrected via an internal function.

Steady-State Fluorescence Quenching. Approximately 200 mg of sample solution were degassed in a septum-capped fluorescence cuvette; a quencher solution was likewise degassed. The emission spectrum was then recorded as described previously. Intensities of the (0,2) (monomer, 400 nm) band were recorded in the absence of quencher (I_0). A microliter syringe was used to deliver aliquots, generally 1–3 μL, of the quencher solution to the sample. The sample cuvette was shaken, and the diminished values of fluorescence intensity were recorded. A positive inert gas pressure was maintained in both the cuvette and quencher vials in order to exclude oxygen.

Transient Fluorescence Studies. A Photochemical Research Associates (PRA) single-photon-counting instrument equipped with a H_2-filled 510-B flashlamp was used to obtain fluorescence decay curves. Fluorescence decay times were fit from decay profiles using either a Digital Micro PDP-11 or an IBM PC. In either case, PRA software was used which employs a nonlinear iterative deconvolution technique to analyze decay curves.

Sample degassing was as described previously. Pyrenesulfonamide-labeled materials were excited at 340 nm; decays were measured at 400 nm (monomer emission) or 519 nm (excimer emission). We have found it important to use a minimal time-per-channel setting to avoid placement of counts in the lower time decades. An appropriate setting for these materials is 0.1786 ns/channel for a range of 512 channels; 10^4 counts were generally taken in the maximum channel.

Transient Fluorescence Quenching Studies. Sample handling was as described for the steady-state quenching experiments, except 400 mg of sample solution was employed. Excitation was at 340 nm; fluorescence decay profiles of the 400-nm (monomer) band were obtained as a function of the quencher concentration.

Results and Discussion

Model Compound Photophysics. To assist in analyzing the photophysical properties of synthetic copolymers 1 and 2 containing the pyrenesulfonamide monomer, we prepare water-soluble model compounds 3 and 4 with the pyrenesulfonamide chromophore. The solubility of compound 4 in water is limited to 3×10^{-5} M despite the hydrophilic gluconamide group. Likewise the solubility of 3 is 6×10^{-5} M at pH 7. At higher pH values the salt is more soluble (1×10^{-2} M).

The UV absorption spectra of 3 and 4 in deionized H_2O are displayed in Figure 1 for comparative purposes. These spectra are essentially identical, as would be expected since both possess the same chromophore. Steady-state fluorescence spectra of 3 and 4 (Figure 2) were recorded upon excitation at 340 nm, over the range 350–600 nm. The three peak maxima characteristic of the monomer emission are 380 (0,0), 400 (0,2), and 418 nm (0,3). In the concentration regime employed (10^{-5} M), the solutions are sufficiently dilute to preclude the formation of excimer. The fluorescence spectrum of a concentrated (ca. 10^{-2} M) aqueous solution of the sodium salt of 3 is shown in Figure 3. The structureless red-shifted emission centered at about 520 nm can be assigned to excimer which forms at higher concentration levels. It should be noted that the salt of 3 may have surfactant characteristics which contribute to excimer formation.

The sulfonamide proton of the pyrenesulfonamide group is acidic; sulfonamides typically have pK_a values ranging from 10 to 12. The effect of pH on the emission was examined by recording fluorescence spectra of 3 (6×10^{-5}

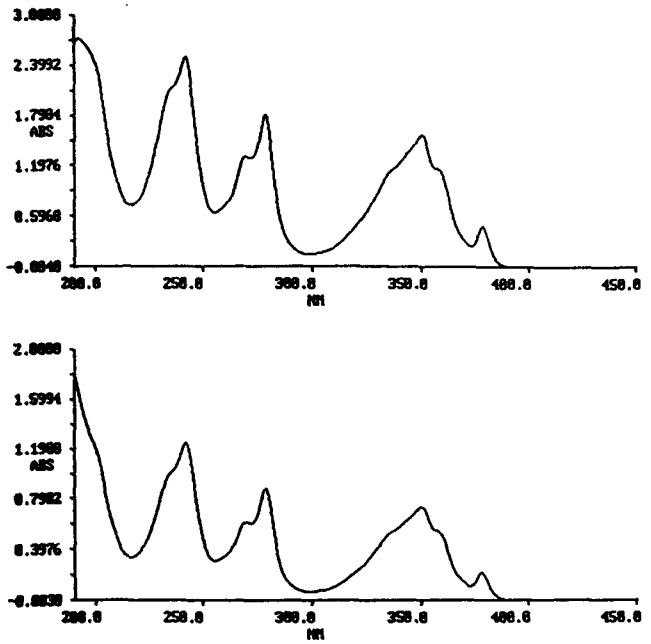


Figure 1. UV absorption spectra of 3 (top) and 4 (bottom) in deionized H_2O ($C = 10^{-6}$ M).

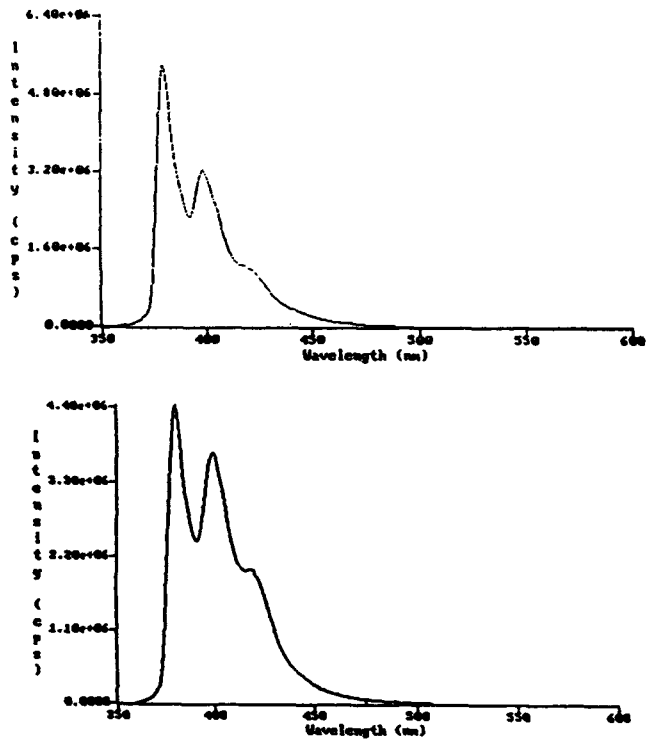


Figure 2. Steady-state fluorescence spectra of 3 (top) and 4 (bottom) in deionized H_2O ($C = 10^{-6}$ M).

M) at pH 10.6 and 12.1. The intensity of the spectrum at pH 12.1 was one-third of that at pH 10.6. The spectral shapes were identical. The diminished intensity of the spectrum acquired at higher pH is likely due to a lack of fluorescence from the sulfonamide anion. Use of this label as a fluorescent tag must therefore be limited to media of pH < 10.

Polymer Absorption and Steady-State Emission Spectra. UV Absorption Spectrum. Figure 4 shows the UV absorption spectra of pyrenesulfonamide-labeled polymers 1 and 2 in deionized H_2O. The absorption spectra above 220 nm are qualitatively identical to those for the model compounds 3 and 4 in Figure 1. This is evidence that the pyrenesulfonamide label has maintained its

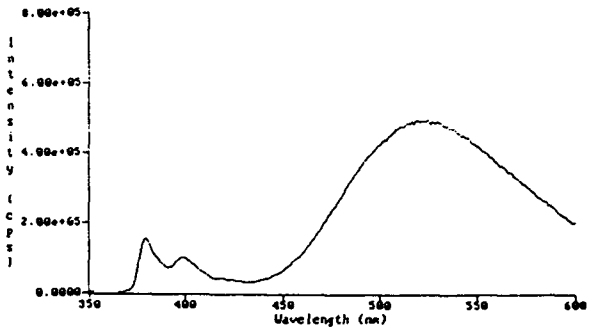


Figure 3. Steady-state emission spectrum of 3 (sodium salt, C = ca. 10^{-2} M) in deionized H_2O.

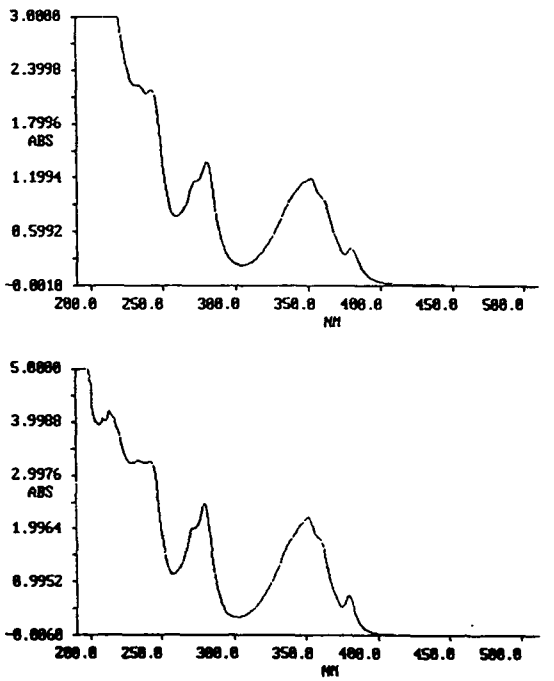


Figure 4. UV absorption spectra of 1 and 2 in deionized H_2O (C = 0.15 g/dL).

integrity during the polymerization process. However, the polymer absorption spectra in Figure 4 are red-shifted compared to those of the model compounds (Figure 1). Comparison of Figures 1 and 4 reveals that the polymer absorption extends to 400 nm; the model compounds, however, fail to absorb appreciably at wavelengths longer than 390 nm. The significance of this effect will be further discussed in a later section.

Steady-State Emission. Steady-state emission spectra of surfactant-polymerized 1 and solution-polymerized 2 are shown in Figure 5. Both labeled polymers display the three peaks assigned to monomer emission, as shown for the model compounds in Figure 2. Excimer emission—centered around 519 nm—is also observed for the labeled polymers. Excimer emission is definitely a polymer-enhanced effect, since the content of the label is 7×10^{-5} M for copolymer 1 and 9×10^{-5} M for copolymer 2. No excimer intensity was observed for the model compounds in this concentration range (Figure 2).

Although 2 contains slightly more pyrenesulfonamide label (0.35 mol % for 2 and 0.25 mol % for 1), the excimer emission intensity of 1 is dramatically enhanced relative to 2. A greater *local concentration* of the label therefore exists for 1 relative to 2, strongly suggesting that microstructural differences exist between these polymers. We believe that copolymer 2, prepared in homogeneous solution, has a more random structure than surfactant-

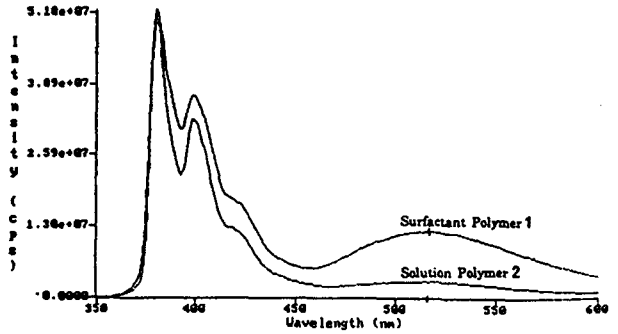


Figure 5. Steady-state emission spectra of 1 (copolymer C = 218 mg/dL; fluorophore $C = 7.13 \times 10^{-6}$ mol L) and 2 (copolymer C = 193 mg/dL; fluorophore $C = 9.28 \times 10^{-6}$ mol/L) in deionized H_2O.

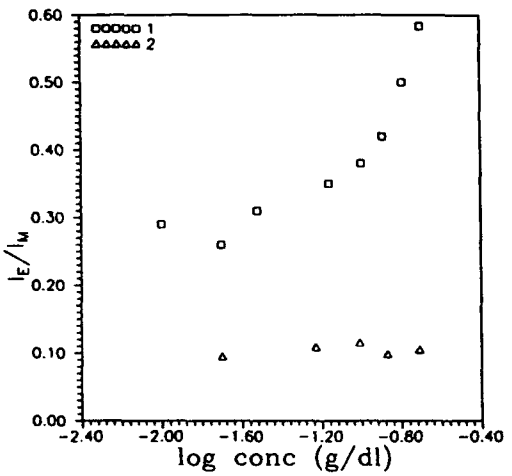


Figure 6. I_E/I_M as a function of the log concentration of 1 and 2 in deionized H_2O.

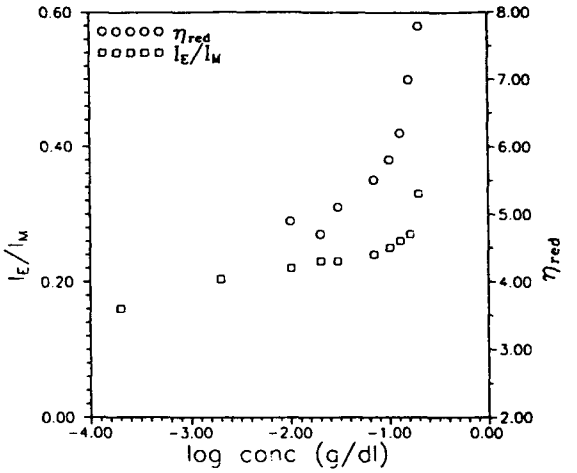


Figure 7. η_{red} and I_E/I_M as a function of the log concentration for 1 in deionized H_2O.

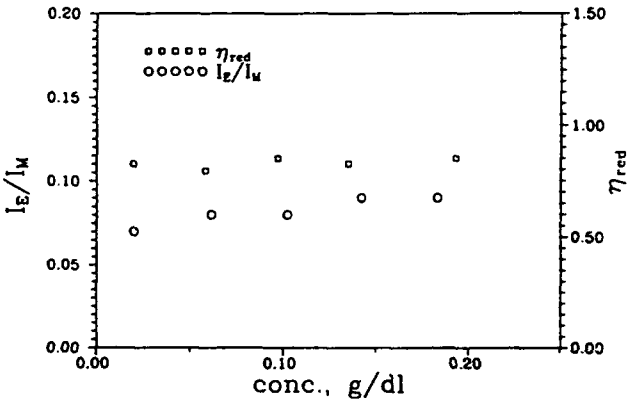


Figure 8. η_{red} and I_E/I_M as a function of the concentration for 2 in deionized H_2O.

polymerized 1, which possesses a blocky microstructure.[35] The microheterogeneous surfactant produces partitioning of the hydrophobic pyrenesulfonamide monomer within the micelle during copolymerization, allowing some degree of blockiness even at low feed composition. Clearly the number of consecutive pyrenesulfonamide label repeat units is determined to some extent by the pyrenesulfonamide monomer label-to-surfactant ratio. Effects of surfactant polymerization methods upon the polymer microstructure have been noted elsewhere. In separate studies, Peer[18] and Dowling and Thomas[19] investigated copolymers synthesized from acrylamide and a hydrophobic comonomer by a surfactant copolymerization technique. The microstructures of these systems are also believed to have blocky characteristics. The copolymers demonstrated either intra- or intermolecular solution behavior,[18] apparently depending upon the choice of hydrophobic comonomer, polymerization conditions, and other factors.

The concentration dependence of excimer-to-monomer ratios, I_E/I_M, for the two copolymers is shown in Figure 6. The concentrations of the polymers were viewed over a range of 10^3, from 2.0×10^{-4} to 0.2 g/dL. The concentration dependences of I_E/I_M values are dramatically different. The I_E/I_M values for 2, the polymer synthesized in homogeneous solution, show only a small concentration dependence, signifying little or no change in the pyrene environment and therefore in polymer conformation. However, I_E/I_M values for 1, the polymer synthesized in the presence of surfactant, increase dramatically at concentrations above ca. 0.1 g/dL, indicating that the pyrene groups are in an increasingly hydrophobic environment presumably caused by increasing intermolecular associations.

The increases of I_E/I_M values with polymer concentration (Figure 6) are paralleled by changes in viscosity, a bulk or macroscopic property. In Figure 7, I_E/I_M and the reduced viscosity of copolymer 1 are plotted as a function of concentration. Viscosity and I_E/I_m *both* increase dramatically above an initial concentration, C^* (ca. 0.1 g/dL), providing strong evidence that intermolecular hydrophobic associations of the pyrenesulfonamide labels are responsible. As concentration increases, intermolecular hydrophobic association of the labels is facilitated. It has been proposed that hydrophobic molecules can locate each other at distances greater than 100 Å due to the strong influence of water-structuring.[20-22] This is reflected on a molecular level by enhancement of I_E/I_M values. On a macroscopic scale, hydrophobic associations are indicated by a sharp increase in the viscosity profile at C^*. To our knowledge, this represents the first associative thickener which relies on a fluorescence label as the sole hydrophobic moiety. Also, the parallel response of I_E/I_M and η_{red} vs concentration (Figure 8), along with previous literature studies, allows rational suggestions to be made on the mode of the micellar or surfactant polymerization, as well as the nature of the aggregation responsible for the associative thickening phenomenon.

Concentration dependencies of η_{red} and I_E/I_M are shown in Figure 8 for copolymer 2 prepared in DMF/H_2O. The zero Huggins constant of the reduced viscosity vs concentration curve suggests a compact polymer conformation that is independent of polymer concentration. The I_E/I_M values confirm this premise. The microstructure of this

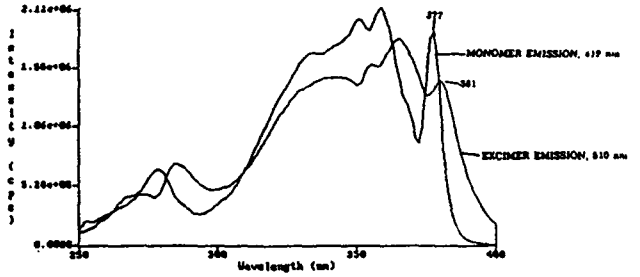


Figure 9. Excitation spectrum at monomer and excimer emissions of 1 in deionized H_2O, C = 0.22 g/dL.

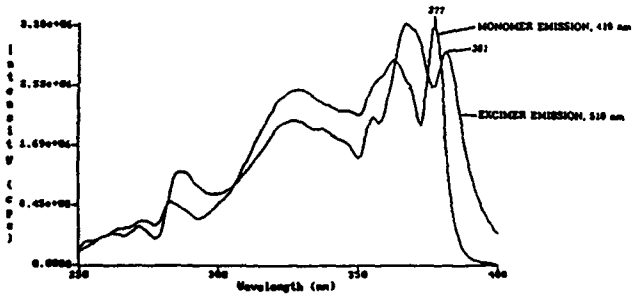


Figure 10. Excitation spectrum at monomer and excimer emissions of 2 in deionized H_2O, C = 0.19 g/dL.

polymer—random label distribution—no doubt strongly influences the polymer conformation. In water, the hydrophobic labels are compelled to aggregate by the hydrophobic effect. The random interspacing of the hydrophobe along the polymer backbone leads to compaction of the polymer coil due to intramolecular associations. Such a compact structure is reflected in the viscosity profile of 2, as we have shown.

In order to further elucidate the nature of the hydrophobic associates, additional studies were conducted. Excitation spectra for polymers 1 and 2 are shown in Figures 9 and 10, wherein emission was monitored at both monomer (419 nm) and excimer (510 nm) wavelengths. In each case, the excitation spectrum of the excimer emission is red-shifted by 4 nm from the monomer excitation spectrum. This suggests that preformed, ground-state aggregates of the pyrenesulfonamide labels are the source of excimer emission. The loss of vibrational structure is consistent with ground-state association.

Typically, in polymer systems, excimer emission results from chromophores which encounter one another through a diffusional process. A chromophore absorbs light, is promoted to the excited state, and, during its excited-state lifetime, encounters a ground-state chromophore. In this case, monomer and excimer excitation spectra are identical, since the initial absorbing species are identical. In our case, however, hydrophobic associations of the pyrenesulfonamide label appear to facilitate the formation of ground-state aggregates. Hydrophobic interactions of the pyrenesulfonamide labels provide a means for facilitating perturbation of the ground state and yielding a species of lower energy. This results in a red-shift in both the absorption spectrum and the excitation spectrum when emission is monitored in the excimer or, perhaps more appropriately, excited aggregate region.

The phenomenon of pyrene absorption and excitation spectral shifts in the context of ground-state interactions has been previously documented. In a fundamental study, Avis and Porter[23] examined the photophysics of pyrene dissolved in a poly(methyl methacrylate) matrix as a function of pyrene concentration. At pyrene concentrations ≥0.01 mol dm^{-3}, excimer emission was observed and

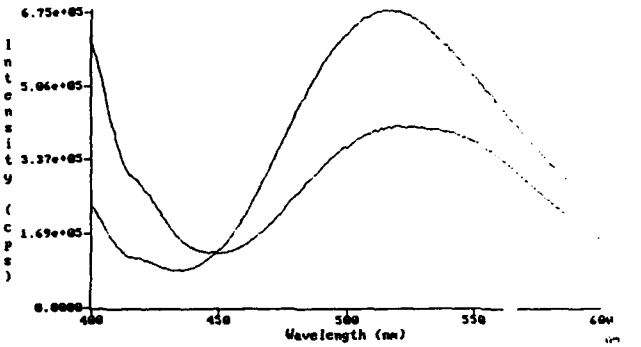


Figure 11. Steady-state emission spectra of 1 and 2 in deionized H_2O (excitation of aggregates at 395 ± 1 nm); concentrations as in Figure 5.

absorption and excitation spectra were red-shifted relative to the spectra of pyrene at lower concentrations. van der Waals interactions of proximate pyrene molecules, resulting in aggregates of lower ground-state energy, were proposed to explain the observed spectral shifts.

Precedence also exists for the aggregation of pyrene-labeled, water-soluble polymers in aqueous media. Winnik and co-workers[7-10] have studied the aggregation behavior of pyrene-labeled (hydroxypropyl)celluloses in water. Excimer excitation spectra were red-shifted relative to monomer excitation spectra, indicating ground-state interactions of the pyrene labels. No rise times were observed for the decay profiles, verifying the preformed nature of the aggregate. Frank and co-workers[6] have reported similar results for pyrene-end-labeled poly(ethylene glycol) in H_2O. In both Winnik's and Frank's studies, comparative spectroscopic studies of pyrene-labeled polymers were performed in methanol as well as in water. No ground-state aggregation of the label moieties was observed in methanol, thus emphasizing the importance of the hydrophobic effect.

Additional evidence for aggregation in polymers 1 and 2 was obtained by excitation of aqueous solutions of 1 and 2 (Figure 11) at 395 nm. Emission in the monomer region is very low for both polymers (compare with Figure 6). The broad red-shifted emission dominates, indicating that indeed the pyrene aggregate is responsible for excimer emission in solutions of 1 and 2. The small amount of monomer emission which seems to be present could be due in part to dissociation of the excited aggregate.

Transient Emission Studies. Analysis of Transient Decay. Background. The Birks[24,25] scheme for excimer formation/dissociation indicates that monomer fluorescence decays as the sum of two exponential terms while the excimer decay can be described as the difference of two exponential terms. The Birks kinetic scheme adequately describes the transient decay behavior of low molar mass systems and some model polymer systems. However, many labeled polymer systems exhibit a complex decay response, and this has been our experience with both 1 and 2.

The fluorescence decay profiles of the models in water or dioxane are monoexponential (Table I). The difference in the lifetimes in water (ca. 13 ns) and dioxane (ca. 30 ns) is quite large, demonstrating the effect of microenvironmental polarity on the decay of the excited state.

The decay profiles of the two polymers 1 and 2 in aqueous solution were complex but could be approximately fit by a sum of two exponentials. In both cases, the decay curve could be fit to a longer-lived component (ca. 15 ns) and a shorter-lived component (ca. 11 ns). Detailed interpretation is impossible, probably because labels in many

Table I
Fluorescence Lifetimes of Model Compounds in Homogeneous Solution[a]

sample	solvent	C, M	T, ns
3	H_2O	2.5×10^{-7}	13.3
	dioxane	2.6×10^{-7}	30.9
4	H_2O	3.1×10^{-7}	13.1
	dioxane	3.1×10^{-7}	30.3

[a] Excitation at 340 nm; monitoring at 400 nm.

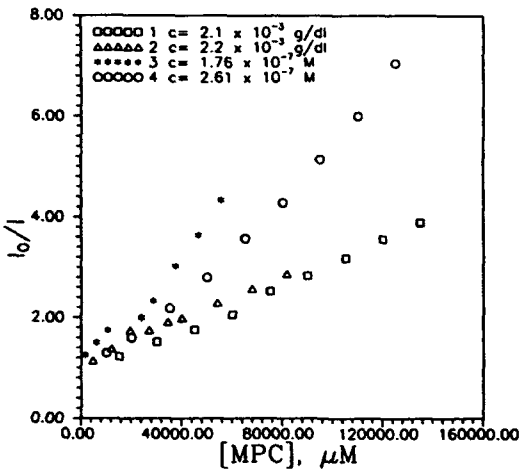


Figure 12. MPC quenching of pyrenesulfonamide polymers and models.

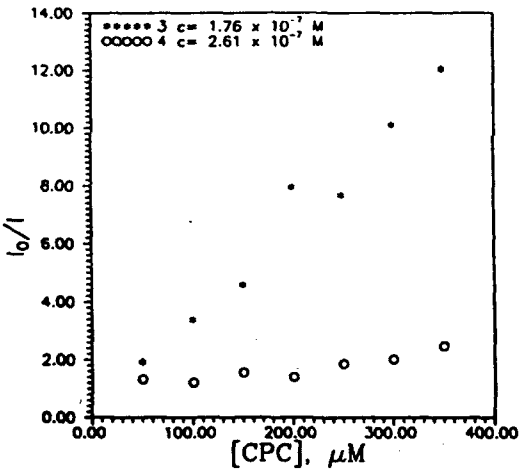


Figure 13. CPC quenching of pyrenesulfonamide models (label concentration $\approx 10^{-6}$ M).

different environments are contributing to the emission decay. One point, however, is particularly informative. The decay profile of the monomer emission (400 nm) of 1 is invariant, within experimental error, with change in the concentration from 2.2×10^{-3} to 2.2×10^{-1} g/dL. However, as noted previously, both the reduced viscosity and the I_E/I_M ratio of 1 increase at concentrations on the order of 2.2×10^{-1} g/dL (Figure 7). It appears as though the local environment of the species responsible for emission at 400 nm in 1 is modified little, if at all, as polymer aggregation occurs.

While it is difficult to interpret the excimer decay profile of the polymer samples, it is worth noting that the excimer decay profiles of 1 and 2 obtained at 550 nm do not exhibit a rise time (characteristic of the diffusion time for excimer formation). The rise times at 550 nm (excimer or excited aggregate emission region) and 400 nm (monomer emission region) are essentially identical. Although specific decay times were not obtained, in general, we note that the decay profile has a long-lived decay component

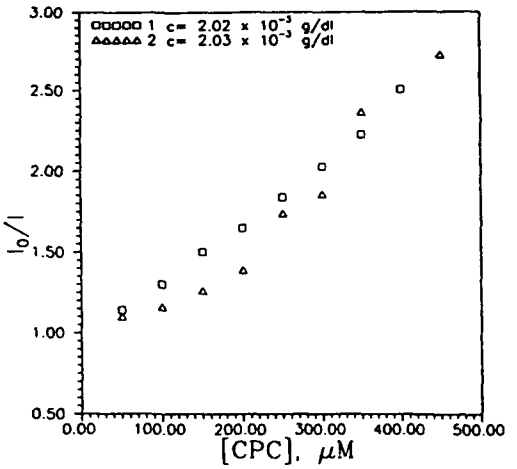


Figure 14. CPC quenching of pyrenesulfonamide polymers (label concentration $\approx 10^{-7}$ M).

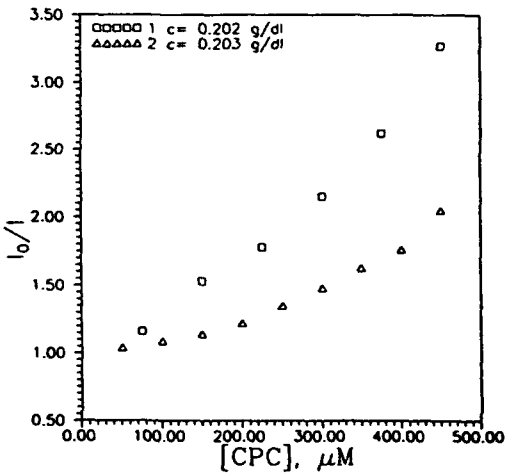


Figure 15. CPC quenching of pyrenesulfonamide polymers (label concentration $\approx 10^{-4}$ M).

on the order of 30 ns. The decay profiles in the excimer region suggest the presence of a ground-state dimer. This idea is supported by the work of Wang et al.,[26] who performed picosecond excimer fluorescence spectroscopy on poly(1-pyrenylmethyl methacrylate) in chloroform. In this study an essentially instantaneous rise was observed for the excimer fluorescence profile on a picosecond time scale, signifying ground-state interactions of the pendent pyrene moieties.

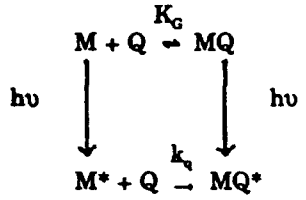
For pyrene-labeled (hydroxypropyl)cellulose, Winnik et al.[7] also identified ground-state pyrene aggregates via excitation spectra and the lack of a rise time for the excimer decay. Frank and co-workers[27] also attributed the emission of pyrene-end-labeled PEG to excitation of preformed pyrene aggregates.

Quenching Studies. In order to further probe the microenvironment of the pyrene fluorophore, the fluorescence of the polymers and the model compounds was quenched by nitromethane (N), iodide ion (I), methylpyridinium chloride (MPC), and cetylpyridinium chloride (CPC). In the case of N and I, quenching data fit the Stern–Volmer equation (eq 1),

$$I_0/I = 1 + K_{SV}[Q] \quad (1)$$

where $K_{SV} = k_Q\tau_0$, I_0 = emission intensity in the absence of quencher, Q, I = emission intensity in the presence of Q, [Q] = quencher concentration, K_{SV} = Stern–Volmer quenching constant, k_Q = quenching rate constant, and τ_0 = lifetime of unquenched fluorophore such that plots

Scheme I
Simple Kinetic Model for Static and Dynamic Quenching of a Fluorophore, M, by a Quencher, Q



("Stern–Volmer plots") of I_0/I vs [Q] were linear for [Q] < ca. 0.01 M. The same plots for MPC and CPC quenching frequently showed upward curvature (Figures 12–15), even at low concentrations of Q, indicative of both static (complexation of Q to fluorophore) and dynamic quenching processes. Attempts to fit these curved plots using several currently available kinetic treatments[36,37] failed. Thus, we will discuss the results using the *simplest* possible kinetic model (Scheme I) for static plus dynamic quenching of a fluorophore M, by Q, in which K_G is the association constant for formation of the complex, MQ. Provided the extinction coefficients of M and MQ at the wavelength of excitation are the same (i.e., Q does not significantly perturb the absorption spectrum of M), the excited complex MQ* is nonfluorescent, and MQ* does not revert significantly to M*, then the modified Stern–Volmer expression (eq 2) holds.[29] This reduces to eq 3 for purely static quenching ($K_{SV} = 0$). This has the same I_0/I vs [Q]

$$I_0/I = 1 + (K_{SV} + K_G)[Q] + K_{SV}K_G[Q]^2 \quad (2)$$

$$I_0/I = 1 + K_G[Q] \quad (3)$$

dependence as purely dynamic quenching but can be distinguished from the latter by measurement of the fluorophore lifetime in the absence (τ_0) and presence (τ) of Q for which eq 4 applies. Thus, for purely dynamic quench-

$$\tau_0/\tau = 1 + K_D[Q] \quad (4)$$

ing $K_{SV} = K_D$, whereas for purely static quenching $K_D = 0$; i.e., the fluorophore lifetime is independent of [Q], although the fluorescence intensity drops as [Q] increases. Finally, from eq 2, the slopes of upwardly curving Stern–Volmer plots should tend to a value of $K_{SV} + K_G$ as [Q] approaches 0.

Stern–Volmer constants (K_{SV}) for the quenching of monomer emission at 400 nm by N, an amphiphilic quencher, and I, an anionic heavy-atom quencher, are given in Table II. From the known lifetimes (τ_0) of the fluorophores (Table I) of the model compounds, both N and I quench fluorophore fluorescence at or near the diffusion-limited rate ($k_Q = (4–7) \times 10^9$ M^{-1} s^{-1}). Exact quenching constants (k_Q) were not calculated for polymers 1 and 2 since a single fluorescence lifetime was not obtained for these materials. However, it is worth noting that K_{SV} values for models 3 and 4 are consistently greater than those for the polymer-bound labels. The (approximately) two-component fluorescence decay of the polymers, with $\tau \simeq 15$ and 11 ns, has a similar "average" lifetime to the single-component decay ($\tau_0 \simeq 13$ ns) of the models (Table I), suggesting k_Q for the polymers is 2–4 times smaller than k_Q for the models. This is attributable to the bulk of the polymers and the enhanced viscosity of the medium. The approximate k_Q values for the polymers (ca. (1–4) × 10^9 M^{-1} s^{-1}) are in the range of being diffusion limited and indicate ready accessibility of these quenchers to the pyrene label.

Table II
Quenching of the Fluorescence[a] of Polymers 1 and 2 and Model Compounds 3 and 4 by Nitromethane (N) and Sodium Iodide (I) in Water

compound	Q	[polymer], g/dL	[label], M	K_{SV}, M^{-1}	k_Q, M^{-1} s^{-1}
3	N		2.5×10^{-8}	49	3.7×10^9
4	N		3.1×10^{-7}	58	4.4×10^9
1	N	2.18×10^{-1}	7.1×10^{-5}	11	
1	N	2.18×10^{-3}	7.1×10^{-7}	23	
2	N	1.93×10^{-1}	9.3×10^{-5}	12	
2	N	1.93×10^{-3}	9.3×10^{-7}	17	
3	I		1.8×10^{-7}	74	5.6×10^9
4	I		2.6×10^{-7}	85	6.5×10^9
1	I	2.0×10^{-3}	6.5×10^{-7}	49	
2	I	2.2×10^{-3}	1.1×10^{-6}	43	

[a] Excitation at 340 nm; quenching at 400 nm.

Table III
Quenching of the Fluorescence[a] of Polymers and Model Compounds by Methylpyridinium Chloride (MPC) and Cetylpyridinium Chloride (CPC) in Water

compound	Q	[polymer], g/dL	[label], M	slope, M^{-1}	K_D, M^{-1}
3	MPC		1.8×10^{-7}	58[b]	
3	CPC		1.8×10^{-7}	35000[b]	
4	MPC		2.6×10^{-7}	36[b]	35
4	CPC		2.6×10^{-7}	4000[b]	60
1	MPC	2.0×10^{-3}	6.5×10^{-7}	18[c]	
2	MPC	2.2×10^{-3}	1.1×10^{-6}	20[c]	
1	CPC	2.0×10^{-3}	6.5×10^{-7}	3800[c]	
2	CPC	2.0×10^{-3}	1.0×10^{-6}	1900[b]	
1	CPC	2.0×10^{-1}	6.5×10^{-5}		
2	CPC	2.0×10^{-1}	1.0×10^{-4}		

[a] Excitation at 340 nm; monitoring at 400 nm. [b] Nonlinear Stern–Volmer plots. The slope is at the linear portion at low Q. [c] Slopes at linear Stern–Volmer plots.

In order to further probe the hydrophobicity of the labeled polymers, CPC, a hydrophobic quencher, was employed for intensity quenching. CPC is a surfactant with a critical micelle concentration (cmc) of 8×10^{-4} M;[28] its pyridinium ring is an oxidative quencher. For comparative purposes, *N*-methylpyridinium chloride (MPC), a less hydrophobic analogue of CPC, was also used.

Figures 12–15 are the monomer intensity quenching curves (Stern–Volmer plots) of the pyrenesulfonamide model compounds and labeled polymers for the alkylpyridinium quenchers. Quenching of the fluorescence of 1 and 2 by CPC is shown for two label concentrations (Figures 14 and 15). In no instance did we observe evidence of exciplex formation in either absorption or emission spectra. Many of the plots show upward curvature. This is probably indicative of a combined static and dynamic quenching process. In the case of MPC quenching of the fluorescence of 3 and 4 (Figure 12), the curvature of the plots is less pronounced than that for CPC, despite the fact that concentrations of MPC were typically over 100 times greater than those for CPC. Stern–Volmer plots for MPC quenching of the fluorescence of 1 and 2 (Figure 12) are essentially linear. In all other cases we estimated the initial slopes of I_0/I vs [Q] plots. Some experiments were also conducted in which fluorophore lifetimes were measured in the presence of Q in order to obtain K_D and k_Q via eq 4.

A summary of the data for fluorescence quenching of 1–4 by MPC and CPC is given in Table III. In the case of the fluorescence of 3 quenched by CPC (Figure 13) a very large initial slope (35 000 M^{-1}) was obtained. This is attributed to complexation of the large hydrophobic carboxylate anion of 3 (a carboxylic acid, but above its

pK) with the large hydrophobic cation CPC. Quenching of the fluorescence of 4 by MPC (Figure 12) must be almost entirely a dynamic process since $K_{SV} \simeq K_D \simeq 35\ M^{-1}$. The quenching rate constant for this process is $2.7 \times 10^9\ M^{-1}\ s^{-1}$ since $\tau_0 = 13.1$ ns for 4 in deionized H_2O (Table I). In contrast, CPC quenching of the fluorescence of 4 (Figure 13) gave an initial slope of $4000\ M^{-1} \gg K_D = 60\ M^{-1}$, indicating a large component of static quenching by CPC. Since 4 is neutral (in contrast to 3), its association with CPC is hydrophobically driven. A hydrophobic salt is formed which is nonfluorescent and leads to predominantly static quenching, in contrast to MPC, which quenches by a purely dynamic mechanism. For CPC quenching of the fluorescence of 4 a value of $k_Q = 4.6 \times 10^9\ M^{-1}\ s^{-1}$ can be obtained from K_D and τ_0. Thus, dynamic quenching of the fluorescence of 4 by both MPC and CPC occurs at near-diffusion-limited rates.

The analysis of MPC and CPC quenching data for the polymers 1 and 2 is hindered by the complex fluorescence decay behavior of the label in the polymer. This precludes our obtaining k_Q values for the polymers using eq 4. However, careful examination of the Stern–Volmer plots of I_0/I vs [Q] leads to some intriguing conclusions. Thus, MPC quenching of the fluorescence of 1 and 2 (Figure 12) gives essentially identical, linear Stern–Volmer plots with slopes of 18 and 20 M^{-1}, respectively. The linear plots indicate either purely dynamic (slope = K_{SV}) or purely static (slope = K_G) quenching. Concentrations of MPC in the same range used for the I_0/I vs [Q] experiments, markedly reduced the (nonexponential) decay of the fluorescence of 1 and 2.[38] Although it is not meaningful to obtain a k_Q value for such a nonexponential decay, this result indicates that MPC quenches the fluorescence of the polymers by a predominantly dynamic, diffusional process. In this respect MPC is analogous to both N and I in its quenching behavior. Once again, the lower values of K_{SV} for polymers 1 and 2 relative to models 3 and 4 can be attributed to the bulk of the polymers and the enhanced viscosity of the medium.

CPC quenching of the fluorescence of low concentrations of 1 and 2 (Figure 14) gives quite a different result from MPC quenching. The Stern–Volmer plot for the surfactant polymer 1 plus CPC is approximately linear with a slope of ca. $3800\ M^{-1}$ for [CPC] < ca. 4×10^{-4} M, whereas the plot for the solution polymer 2 plus CPC is distinctly curved upward over the same range of [CPC] with a much lower initial slope of ca. $1900\ M^{-1}$. The near linear plot for [CPC] and its high slope must be a consequence of predominantly static quenching with $K_G \simeq 3800\ M^{-1}$. Assumption of dynamic quenching (i.e., $K_{SV} \simeq 3800\ M^{-1}$) would lead to an unreasonably high k_Q of ca. $3 \times 10^{11}\ M^{-1}\ s^{-1}$ if $\tau_0 = 13$ ns is assumed for the polymer. Indeed, the slope of $3800\ M^{-1}$ for 1 plus CPC is very similar to the value of $4000\ M^{-1}$ obtained for neutral model 4 plus CPC. We note that the (nonexponential) fluorescence decay is minimally affected by addition of CPC quencher relative to MPC, thus verifying the static nature of the CPC–polymer label interaction.[38] Presumably association of both 1 and 4 with CPC is hydrophobically driven. The solution polymer 2 also gives a large but lower initial slope ($1900\ M^{-1}$) of the Stern–Volmer plot for CPC quenching. The lower initial slope indicates less complexation, and the curvature of the plot suggests a larger contribution of dynamic quenching for this polymer with randomly spaced pyrene labels. Stern–Volmer plots for quenching of the fluorescence of higher concentrations of 1 and 2 by CPC are shown in Figure 15. Both plots show marked upward curvature most probably a consequence of the CPC concentrations (up to 5×10^{-4} M) being comparable to label concentrations. Once again the effect of CPC on the fluorescence of 1 is greater than that on the fluorescence of 2 at low [CPC], suggesting the surfactant quencher interacts more strongly with polymer 1, which has blocks of hydrophobic pyrene labels. Thus hydrophobically modified polymers form (static) hydrophobic aggregates with surfactants such as CPC, even below the critical micelle concentration of the surfactant. Formation of such aggregates is the dominant mechanism of fluorescence quenching by CPC, the effect being most striking for the surfactant polymer 1. Such polymer/surfactant complexes are of interest from both fundamental[30] and practical[31] points of view. It may also be significant that, at low polymer concentrations, K_{SV} for the fluorescence of 1 quenched by CPC is about twice as large as the initial slope for 2 quenched by CPC (recall that K_{SV} values for 1 and 2 plus MPC are essentially identical). This may indicate that the hydrophobic CPC has some preference for association with the blocky regions of 1 rather than the more randomly spaced hydrophobic labels in 2. A number of other groups[1,10,11,32-34] have employed photophysical techniques to observe surfactant interactions with pyrene-labeled polymers. Our study differs in that we have also employed a quenching process to observe these interactions.

Conclusions

This work dealt with the photophysics of pyrenesulfonamide-labeled water-soluble polymers prepared by either a microheterogeneous surfactant copolymerization technique or by a homogeneous solution polymerization technique. The surfactant copolymerization technique yielded a pyrenesulfonamide-labeled copolymer 1, which proved to be a model associative thickener. Viscosity profiles of this polymer in aqueous media exhibit a low critical overlap concentration—typical associative thickener behavior. A blocky microstructural tendency was demonstrated for this polymer from I_E/I_M ratios of the pyrenesulfonamide label. This microstructure is a consequence of the microheterogeneity present during the surfactant copolymerization. Hydrophobic interactions of the label, as evidenced by I_E/I_M, parallel that of the viscosity profile. The viscosity response of the polymer is therefore driven by the molecular, hydrophobic interactions of the pyrenesulfonamide label. These hydrophobic interactions lead to a formation of static, ground-state aggregates of the pyrene labels as denoted by excitation studies and lifetime measurements. Quenching studies of the pyrenesulfonamide label imply that it resides in an open, aqueous environment accessible to hydrophilic quenchers such as iodide ion. The hydrophobic character of the label was verified by its interactions with the hydrophobic CPC quencher; a static hydrophobic complex was formed.

The solution polymerization technique gave a pyrenesulfonamide-labeled copolymer, 2, with largely intramolecular associative behavior. Fluorescence measurements suggested this copolymer has a random microstructure, as would be expected to result from the copolymerization of two acrylamide monomers in a homogeneous medium. The random microstructure of this polymer appears to facilitate a compact conformation due to intramolecular hydrophobic interactions of the interspaced pyrenesulfonamide label. The Huggins profile of this polymer in aqueous solutions has zero slope, demonstrating a compact, noninteracting conformation. On a molecular level, I_E/I_M values are independent of polymer concentration,

paralleling the viscosity response of this system. Associations of the pyrene label are also static. Although the polymer conformation is compact, fluorescence quenching and lifetime measurements suggest the pyrenesulfonamide labels reside in a relatively aqueous microenvironment and are approached and encountered by small molecules at or near the diffusional rate. Quenching of this copolymer with the hydrophobic CPC confirmed the hydrophobic character of the pyrenesulfonamide label and its tendency to form static aggregates via hydrophobic associations in H_2O.

In summary, we have employed photophysical techniques to elucidate the associative behavior of pyrenesulfonamide-labeled polyacrylamides in aqueous media. Correlations between macroscopic (viscometric) and molecular (photophysical) characterization methods have allowed us to develop structure–property relationships for systems in which the pyrenesulfonamide moiety serves as the sole hydrophobe responsible for associative behavior.

Acknowledgment. Research support from DARPA, the Office of Naval Research, the Department of Energy, Unilever, and the National Science Foundation EPSCOR program is gratefully acknowledged.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1992	Journal article

4. TITLE AND SUBTITLE
Water Soluble Copolymers. 41. Copolymers of Acrylamide and Sodium 3-Acrylamido-3-Methylbutanoate

5. FUNDING NUMBERS
C: N00014-89-J-1893

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
The University of Southern Mississippi
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8. PERFORMING ORGANIZATION REPORT NUMBER
91-92-6

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Avenue
Arlington, VA 22217

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Published in J. Macromol. Sci.--Pure Appl. Chem., 1992, A29(3), 193-205

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*
See attachment

14. SUBJECT TERMS

15. NUMBER OF PAGES
13

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Unlimited

J.M.S.—PURE APPL. CHEM., A29(3), pp. 193–205 (1992)

WATER-SOLUBLE COPOLYMERS. XLI. COPOLYMERS OF ACRYLAMIDE AND SODIUM 3-ACRYLAMIDO-3-METHYLBUTANOATE

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ABSTRACT

Copolymers of acrylamide (AM, M_1) with sodium 3-acrylamido-3-methylbutanoate (NaAMB, M_2) synthesized in 1 *M* NaCl (the ABAM2 series) are compared to those synthesized in deionized water (the ABAM1 series). At fixed feed ratios, higher incorporation rates were found for NaAMB with increasing ionic strength of the polymerization solvent. Reactivity ratios calculated by the methods of Kelen-Tüdös changed from $r_1 = 1.23$ and $r_2 = 0.50$ in deionized water to $r_1 = 1.00$ and $r_2 = 0.64$ in 1 *M* NaCl. This change is in accord with a decrease in electrostatic repulsion between the macroradical and unreacted NaAMB. Dilute solution properties, examined as a function of composition and added electrolytes, indicate differences in microstructure for the ABAM1 and ABAM2 copolymers.

INTRODUCTION

Water-soluble polymers that maintain high solution viscosities in the presence of added electrolytes have been the subject of our continuing research [1–3]. We have previously studied the copolymers of sodium 3-acrylamido-3-methylbutanoate (NaAMB, M_2) with acrylamide (AM, M_1) synthesized in deionized water [4, 5]. NaAMB (Fig. 1) is the carboxylated version of the pH stable monomer sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS). These monomers feature two geminal methyl groups that protect the amide functionality from hydrolysis. The

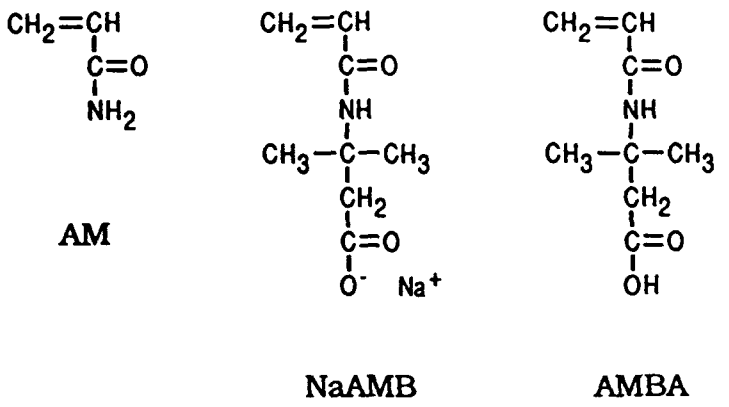

FIG. 1. Structures of comonomers: acrylamide (AM); sodium 3-acrylamido-3-methylbutanoate (NaAMB); and 3-acrylamido-3-methylbutanoic acid (AMBA).

acrylamido functionality allows polymerization to high molecular weights due to a high value of k_p^2/k_t.

Homopolymers of NaAMB and copolymers with AM are chain-extended, water-soluble polymers known for their phase stability in the presence of Na^+ and Ca^{2+} and in high-temperature environments [4, 5]. Their attractive viscosity characteristics and electrolyte tolerance have been attributed to neighboring group and intraunit interactions.

In this study, we examine the effects of changing the ionic strength of the polymerization solvent (water) on polymer microstructure and on solution properties. By synthesizing the homopolymer of NaAMB, and the copolymers with AM, in the presence of electrolytes, we anticipate changes in microstructure and thus in solution behavior [6].

EXPERIMENTAL

Materials and Monomer Synthesis

3-Acrylamido-3-methylbutanoic acid (AMBA) monomer was synthesized via a Ritter reaction of equimolar amounts of 3,3-dimethylacrylic acid with acrylonitrile as reported by Hoke and Robins [7] and modified by McCormick and Blackmon [4]. AM from Aldrich was recrystallized twice from acetone prior to use. Potassium persulfate from Aldrich was recrystallized twice from water prior to use. Reagent-grade sodium chloride from Fisher Scientific was used without further purification.

Synthesis of Copolymers of Sodium 3-Acrylamido-3-Methylbutanoate and Acrylamide in the Presence of NaCl

The ABAM2 series of copolymers was synthesized by free radical polymerization of NaAMB with AM in 1 *M* NaCl solution. These copolymers were compared with the copolymers of the analogous ABAM1 series previously synthesized in deionized water by McCormick and Blackmon [4]. In both cases potassium persulfate

was used as the initiator; the reactions were conducted at 30°C and pH 9 with a 0.46 *M* monomer concentration. For each series the amount of acrylamide in the feed varied from 25 to 90 mol%.

A typical synthesis involved the dissolution of specified quantities of the monomers in separate solutions. The sodium salt NaAMB was obtained by the addition of NaOH to AMBA. The monomers were then mixed to form a single solution. Following adjustment of the pH to 9, the reaction mixture was transferred to a 500-mL, three-necked, round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, and gas bubbler. The mixture was sparged with nitrogen for 20 min and then initiated with 0.1 mol% potassium persulfate. Samples were taken at low and moderate conversions to study copolymer drift. The polymers were precipitated in acetone, redissolved in deionized water, and then dialyzed using Spectra/Por 4 dialysis bags with molecular weight cutoffs of 12,000–14,000 Daltons. After isolation by lyophilization, the copolymers were stored in desiccators. IR: ABAM2-100 homopolymer, N—H (broad), 3400–3300 cm^{-1}; C—H, 2955 cm^{-1}; amide C=O, 1655 cm^{-1}; sodium salt C=O, 1580 cm^{-1}. Typical copolymer: ABAM2-40, N—H (broad), 3450–3300 cm^{-1}; AM amide C=O, 1665 cm^{-1}; NaAMB amide C=O, 1655 cm^{-1}(s), 1520 cm^{-1} (m); sodium salt C=O, 1580 cm^{-1}. ^{13}C NMR: ABAM2-40, Acrylamido C=O, 182.3 ppm; NaAMB C=O, 178.1 ppm; chain CH_2, 38.0 ppm; chain CH, 44.6 ppm; gem CH_3, 29.0 ppm; NaAMB C, 55.4 ppm; NaAMB CH_2, 50.8 ppm.

Copolymer Characterization

Elemental analyses for carbon, hydrogen, and nitrogen were conducted by M-H-W Laboratories (Phoenix, AZ) on both the low- and high-conversion copolymer samples. ^{13}C NMR spectra were obtained using 10 wt% aqueous (D_2O) polymer solutions. The procedure for quantitatively determining copolymer compositions from ^{13}C NMR has been discussed in detail elsewhere [8]. FT-IR spectra for all materials synthesized were obtained using a Perkin-Elmer 1600 Series FT-IR spectrophotometer. Light-scattering studies were performed on a Chromatix KMX-6 low-angle laser light-scattering spectrophotometer, and refractive index increments were obtained using a Chromatix KMX-16 laser differential refractometer. All measurements were conducted at 25°C in 0.512 *M* NaCl at a pH of 7.0 ± 0.1.

Viscosity Measurements

Stock solutions of sodium chloride (0.042, 0.086, 0.257, and 0.514 *M* NaCl) were prepared by dissolving the appropriate amount of salt in deionized water in volumetric flasks. Polymer solutions were then made by dissolution and dilution to appropriate concentrations. After 2–3 weeks of aging, the solutions were analyzed with a Contraves LS-30 rheometer.

RESULTS AND DISCUSSION

Copolymers of NaAMB and AM synthesized in deionized water (the ABAM1 series) are expected to be different from those synthesized in a 1 *M* NaCl aqueous solution (the ABAM2 series). At pH 9, well above the pKa of the carboxylic acid

group, AMBA exists in its charged form, NaAMB (Fig. 1). During polymerization the presence of NaCl should shield electrostatic interactions between charged groups, minimizing charge-charge repulsion between the NaAMB units on the growing macromolecular chain and the unreacted NaAMB.

Effects of NaCl on Composition

Varying comonomer feed compositions were used to synthesize the ABAM2 copolymer series with aqueous 1 *M* NaCl as the polymerization solvent (Table 1). The low conversion aliquots were taken when the reaction mixture first showed signs of increased viscosity. The polymerizations were then allowed to proceed to high conversion for optimum polymer yield. The compositions in Table 1 show a small amount of compositional drift as a result of the increased conversion. For example, the copolymerization conducted at a 60:40 ratio of AM:NaAMB showed a 1.2% increase in M2 composition at 24% conversion over that observed at 4.1% conversion. The copolymers synthesized in deionized water did not exhibit copolymer drift with increased conversion.

Elemental analysis was used to determine the copolymer compositions. The weight percentages of carbon and nitrogen obtained from elemental analysis can be represented by Eqs. (1) and (2).

$$\% \text{ C}/12.01 = 3A + 8B \quad (1)$$

$$\% \text{ N}/14.01 = A + B \quad (2)$$

TABLE 1. Reaction Parameters for the Copolymerization of Acrylamide (AM) with Sodium 3-Acrylamido-3-Methylbutanoate (NaAMB) Synthesized in 1 *M* NaCl

Sample number	Feed ratio (AM:NaAMB)	Reaction time (h)	Conversion (%)	Weight (% C)	Weight (% N)	NaAMB in copolymer (mol%)[a]
ABAM2-10-1	90:10	2.25	8.6	46.47	15.42	9.6 ± 0.2
ABAM2-10-2	90:10	4.42	20.1	45.66	15.08	10.6 ± 0.2
ABAM2-25-1	75:25	1.33	3.8	46.64	12.98	23.8 ± 0.5
ABAM2-25-2	75:25	10.25	14.1	—	—	24.8 ± 1.2[b]
ABAM2-40-1	60:40	1.5	4.1	47.21	11.44	36.3 ± 0.9
ABAM2-40-2	60:40	8.0	24.0	46.46	11.12	37.5 ± 0.9
ABAM2-60-1	40:60	1.5	11.4	47.62	9.83	53.0 ± 1.4
ABAM2-60-2	40:60	4.0	17.8	46.63	9.15	56.4 ± 1.5
ABAM2-75-1	25:75	1.5	8.6	46.87	8.57	67.6 ± 1.9
ABAM2-75-2	25:75	3.0	30.6	45.49	8.15	70.2 ± 1.9
ABAM2-100	0:100	5.42	5.5	44.76	6.27	100[c]
ABAM2-0	100:0	6.5	50.3	—	—	0[c]

[a]Determined from elemental analysis.
[b]Determined from ^{13}C NMR.
[c]Theoretical value.

TABLE 2. Reaction Parameters for the Copolymerization of Acrylamide (AM) with Sodium 3-Acrylamido-3-Methylbutanoate (NaAMB) Synthesized in Solvents of Varying Ionic Strengths at a Fixed Feed Ratio

Sample number	Feed ratio (AM:NaAMB)	Ionic strength (mol/L)	Reaction time (h)	Conversion (%)	Weight (% C)	Weight (%N)	NaAMB in copolymer (mol%)[a]
ABAM2-75(D.I.)	25:75	0.00	2.66	4.0	44.36	8.53	61.3 ± 1.6
ABAM2-75(0.15)	25:75	0.15	2.66	7.1	44.39	8.60	60.4 ± 1.7
ABAM2-75(0.20)	25:75	0.20	4.00	3.5	46.34	8.76	63.4 ± 1.7
ABAM2-75(0.30)	25:75	0.30	3.75	23.6	46.88	8.58	67.5 ± 1.8
ABAM2-75(0.45)	25:75	0.45	2.33	7.0	45.86	8.23	70.0 ± 1.9
ABAM2-75(1.00)	23:75	1.00	1.50	8.6	45.49	8.15	67.6 ± 1.2

[a]Determined by elemental analysis.

The coefficients A and B are the number of moles of AM and NaAMB, respectively, in a normalized amount of copolymer, e.g., 1 g. The mole percent of each monomer in the copolymer may then be determined using Eqs. (3) and (4).

$$\text{mol\% AM} = A/(A + B) \times 100\% \quad (3)$$

$$\text{mol\% NaAMB} = B/(A + B) \times 100\% \quad (4)$$

A second set of copolymers was synthesized in which the ionic strength of the polymerization solvent was varied while the copolymer composition was maintained at 25:75 AM:NaAMB (Table 2). As illustrated in Fig. 2, increasing the ionic strength

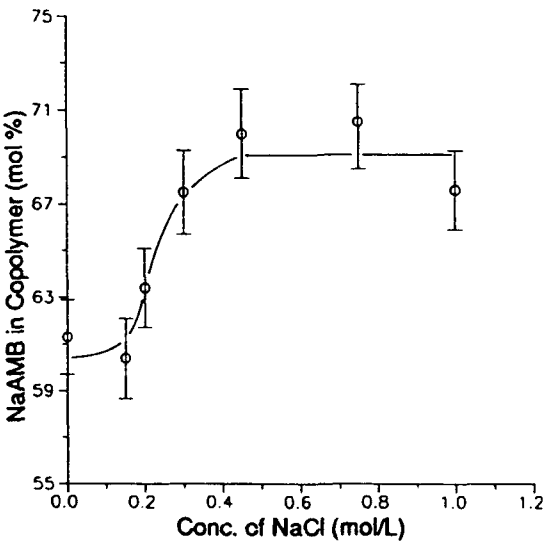

FIG. 2. Mole percent NaAMB incorporated into a copolymer as a function of salt concentration when the feed ratio is kept constant at 25/75 mol% AM/NaAMB.

of the polymerization solvent allows more NaAMB to be incorporated into the copolymers up to a limiting composition. These results are similar to those of Breslow and Kutner [9], who prepared polymers of sodium ethylenesulfonate. They found an increase in the rate of polymerization and molecular weight upon the addition of sodium acetate. This was attributed to the reduction of an electrostatic effect which repels the ionic monomer from the negative charges on the growing chain. The compositions of the copolymers in Table 2 indicate that a similar reduction in electrostatic repulsion has occurred in the presence of NaCl. However, the relative hydrophobic character of NaAMB may also enhance its reactivity with the terminal NaAMB mer on the propagating chain.

Effects of NaCl on Reactivity Ratios

The compositions of the low-conversion copolymers of the ABAM1 and ABAM2 series are compared in Table 3. For every feed composition, the copolymers synthesized in the presence of NaCl had greater amounts of NaAMB incorporated. This information is presented graphically in Fig. 3. The data for the ABAM2 copolymers lie closer to the dashed line, which represents completely random copolymerization. The reactivity ratios (Table 4) derived by the methods of Fineman-Ross [10] and Kelen-Tüdös [11] are closer to "ideal" ($r_1 = r_2 = 1$) with added NaCl; r_1, r_2 values are 1.2, 0.5 in water and 1.0, 0.6 in NaCl solution, respectively. It is interesting that the product $r_1 r_2$ does not change significantly for the copolymers made in the absence or presence of salt (Table 4).

TABLE 3. Compositions of Copolymers of Acrylamide (AM) with Sodium 3-Acrylamido-3-Methylbutanoate (NaAMB) Synthesized in Deionized Water (the ABAM1 series) and in 1 *M* NaCl (the ABAM2 Series)

Sample number	Feed composition (mol%)		Polymer composition[a] (mol%)	
	AM	NaAMB	AM	NaAMB
ABAM1-10-1	90	10	92.0	8.0
ABAM1-25-1	75	25	79.7	20.3
ABAM1-40-1	60	40	68.6	31.2
ABAM1-60-1	40	60	51.6	48.4
ABAM1-75-1	25	75	37.9	63.1
ABAM2-10-1	90	10	90.4	9.6
ABAM2-25-1	75	25	76.2	23.8
ABAM2-40-1	60	40	63.7	36.3
ABAM2-60-1	40	60	47.0	53.0
ABAM2-75-1	25	75	32.4	67.6

[a]Determined from elemental analysis.

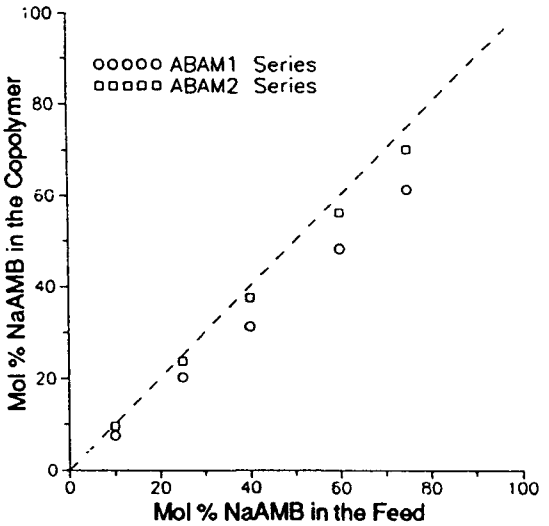

FIG. 3. Mole percent NaAMB incorporated into the copolymers as a function of comonomer feed ratio for the copolymers synthesized in deionized water (ABAM1 series) and in 1 *M* NaCl (ABAM2 series). The dashed line represents $r_1 = r_2 = 1.0$.

Changes in Copolymer Microstructure

Statistical microstructural information can be obtained using the equations of Igarashi [12] and Pyun [13]. These methods allow calculation of the fractions of M_1-M_1, M_2-M_2, and M_1-M_2 units in the copolymers from experimentally determined reactivity ratios and copolymer composition.

The results obtained for the copolymers (Table 5) support the premise that changing the ionic strength of the polymerization solvent should lead to different copolymer microstructures. However, when the number of NaAMB-centered triads is plotted as a function of copolymer composition (Fig. 4), the ABAM1 and ABAM2 series data fall on the same curve. The dashed line represents the triad distribution for an r_1r_2 value of 0.64. Igarashi's equations depend on the inverse of r_1r_2, and as long as this product remains the same, the outcome of the equations will be the same.

Harwood, Park, and Santee discussed the inadequacies of reactivity ratios by examining the microstructure of acrylamide copolymers using a catalyzed intra-

TABLE 4. Reactivity Ratios for the ABAM1 and ABAM2 Copolymer Series Determined Using the Methods of Kelen-Tüdös and Fineman-Ross

	ABAM1			ABAM2		
Method	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2
Kelen-Tüdös	1.23 ± 0.02	0.50 ± 0.04	0.62	1.00 ± 0.03	0.64 ± 0.05	0.64
Fineman-Ross	1.20 ± 0.02	0.47 ± 0.05	0.56	0.98 ± 0.03	0.59 ± 0.05	0.58

TABLE 5. Structural Data for the Copolymers of Acrylamide (AM, M_1) with Sodium 3-Acrylamido-3-Methylbutanoate (NaAMB, M_2) Synthesized in Deionized Water and 1 *M* NaCl

Sample number	NaAMB in copolymer (mol%)	Blockiness (mol%)		Alternation (mol%)	Mean sequence length	
		M_1-M_1	M_2-M_2	(M_1-M_2)	M_1	M_2
ABAM1-10-1	8.0	84.3	0.4	15.3	11.8	1.1
ABAM1-25-1	20.3	62.2	2.8	35.0	4.6	1.2
ABAM1-40-1	31.2	44.8	7.2	48.0	2.8	1.3
ABAM1-60-1	48.4	21.3	19.9	57.0	1.8	1.7
ABAM1-75-1	63.1	10.6	36.8	52.6	1.4	2.4
ABAM2-10-1	9.6	81.4	0.6	18.1	9.8	1.1
ABAM2-25-1	23.8	56.4	4.0	39.6	3.9	1.2
ABAM2-40-1	36.3	37.8	10.4	51.9	2.5	1.4
ABAM2-60-1	53.0	18.7	24.8	56.5	1.7	1.9
ABAM2-75-1	67.6	8.0	43.2	48.8	1.3	2.8

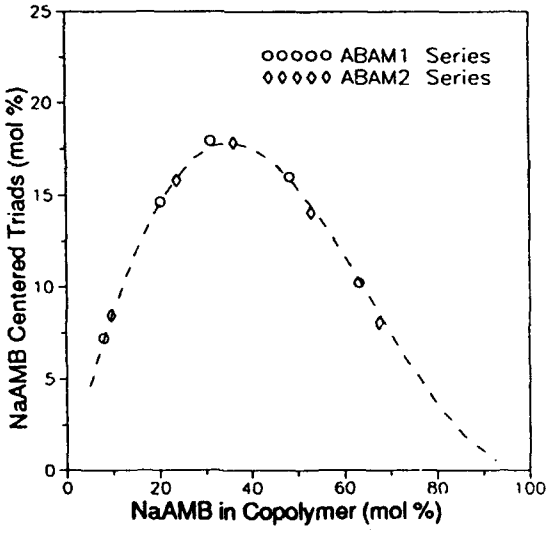

FIG. 4. Number of NaAMB monomer unit centered triads as a function of polymer composition for ABAM1 and ABAM2 copolymers. The dashed line represents the triad distribution for any polymer with $r_1r_2 = 0.64$ regardless of the values of r_1 and r_2.

sequence cyclization technique [14]. They found that synthesizing copolymers of acrylamide with styrene in a variety of solvents led to copolymers with the same microstructure despite extreme differences in reactivity ratios.

Viscometric Studies

Effects of Copolymer Composition

The viscosity data obtained in this work indicate a change in the microstructure of the copolymers after change of the ionic strength of the polymerization solvents. The intrinsic viscosities, obtained from Huggins plots, for the ABAM1 and ABAM2 series copolymers are shown in Fig. 5. For both series, the highest intrinsic viscosities were obtained from the copolymers containing less than 40 mol% of NaAMB. Counterion condensation likely occurs at compositions with more NaAMB. Additionally, decreasing molecular weight occurs with increasing NaAMB incorporation yielding lower viscosities.

The differences in location of the viscosity maxima may be due to neighboring group effects. At certain compositions, the monomer units along the backbone can interact via hydrogen bonding to form chain-stiffening structures [2]. The frequency of these interactions will depend on the polymer microstructure. From Fig. 6 it appears that the highest viscosities in deionized water are produced when the composition of NaAMB lies between 10 and 25 mol% for the ABAM1 series and between 20 and 40 mol% for the ABAM2 series. The lack of smoothness of the viscosity copolymer composition curve from the ABAM1 series has been reported previously and may be due to conformational restrictions due to nearest-neighbor interactions [5].

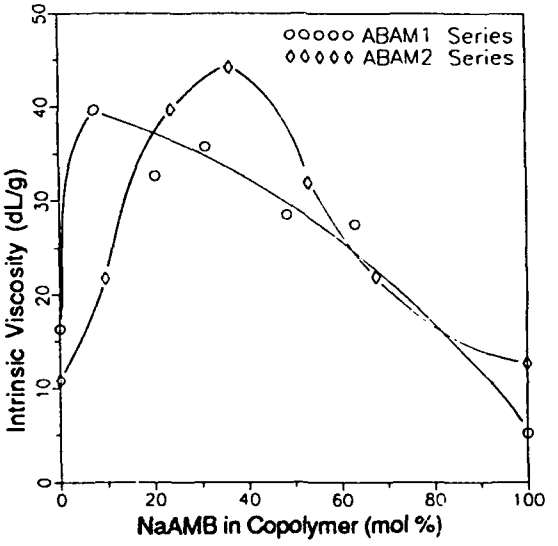

FIG. 5. Compositional effect on intrinsic viscosity for the ABAM1 and ABAM2 copolymer series in 0.514 *M* NaCl determined with a shear rate of 1.75 s^{-1} at 30°C.

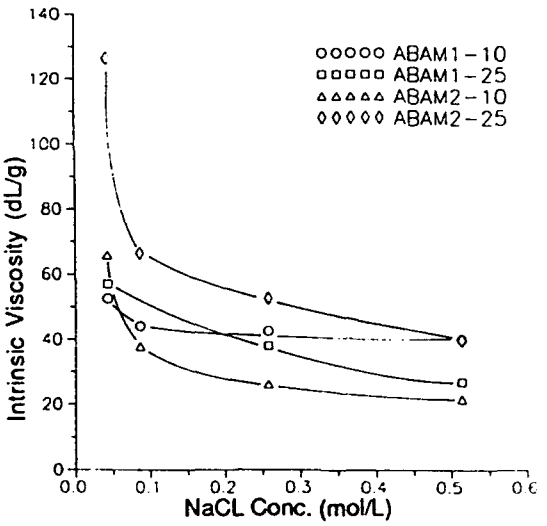

FIG. 6. Effect of sodium chloride concentration on the intrinsic viscosities of ABAM1 and ABAM2 copolymers determined at 30°C with a shear rate of 1.25 s^{-1}

Effects of Molecular Weight

Molecular weight affects the dilute solution behavior of copolymers. Table 6 compares the molecular weights of the copolymers made in deionized and salt water. Samples ABAM1-10-2 and ABAM2-25-2 have molecular weights of 15.6 × 10^6 and 16.0 × 10^6 g/mol, respectively. These two copolymers also have similar zero-shear intrinsic viscosities. Second-virial coefficients indicate that even though ABAM1-10-2 has less charge than ABAM2-25-2, it is better solvated.

Samples ABAM1-25-2 and ABAM2-40-2 also have similar molecular weights, but their viscosities are markedly different. The dissimilar second-virial coefficients indicate the importance of polymer solvation on hydrodynamic volumes in solution.

TABLE 6. Molecular Weight and Second-Virial-Coefficient Data for the ABAM1 and ABAM2 Copolymer Series

Sample number	Composition		MW	A_2
	AM	NaAMB	(× 10^{-6} g/mol)	(× 10^4mL·mol/g^2)
ABAM1-10-2	91.6	8.4	15.6	4.28
ABAM1-25-2	79.9	20.1	12.9	1.52
ABAM1-60-2	50.2	49.8	14.0	3.49
ABAM2-10-2	90.4	9.6	6.8	4.39
ABAM2-25-2	76.2	23.8	16.0	3.60
ABAM2-40-2	63.7	36.3	11.9	4.02

The small A_2 values for both ABAM1-25-2 and ABAM2-25-2 suggest the existence of microstructural interactions like those discussed above.

Effects of Added Electrolytes

The relationship of zero-shear intrinsic viscosity to ionic strength for a number of ABAM1 and ABAM2 copolymers as a function of ionic strength is illustrated in Fig. 6. Typical polyelectrolyte behavior is observed. The polymer chains collapse as the ionic strength of the solvent increases. The change of intrinsic viscosity with ionic strength has been used as a qualitative measure of chain flexibility. Smidsrod and Haug [15] obtained what they called a "stiffness parameter," B, utilizing Eq. (5) in which S is the slope of the plot of $[\eta]$ as a function of the inverse square root of the ionic strength and $[\eta]_M$ is the intrinsic viscosity at a given salt concentration. The exponent r is assumed invariant to polymer type and has an approximate value of 1.3

$$S = B \cdot ([\eta]_M)^r \tag{5}$$

Values of B are generally low for polymers that retain their viscosity (remain extended) with increasing electrolyte concentration. Higher B values are reported for flexible polymers. It should be noted that B is inversely related to measures of stiffness such as persistence length on the steric factor [15]. In general, B values (Table 7) for the copolymers in this work are higher for the ABAM2 series than for the ABAM1 series for similar overall compositions up to 65 mol%. Differences in the aqueous solution viscosities for very similar molecular weights can only be attributed to microstructural differences.

Interestingly, ABAM1-10-2 with 8.4 mol% NaAMB in the copolymer exhibits the best electrolyte tolerance over a wide range of NaCl concentrations consistent

TABLE 7. Comparison of the ABAM1 and ABAM2 Copolymer Series Based on the Smidsrod and Haug Stiffness Parameter

Sample number	NaAMB in copolymer (mol%)	B ($[\eta]_{0.514M}$)
ABAM1-10-2	8.4	0.03
ABAM1-25-2	20.1	0.07
ABAM1-40-2	31.4	0.12
ABAM1-60-2	49.8	0.12
ABAM1-75-2	63.6	0.11
ABAM2-10-2	10.6	0.06
ABAM2-25-2	24.8	0.15
ABAM2-40-2	37.5	0.20
ABAM2-60-2	56.4	0.16
ABAM2-75-2	70.2	0.11

with our previous observations [2, 4, 5]. Neighboring-group interactions between isolated NaAMB units and acrylamide are suggested to be responsible for chain stiffening. More random placement of NaAMB units, as experimentally observed in synthesis from NaCl solutions, leads to higher B values and less stiffening. Finally, above 65 mol% few isolated NaAMB units are available for placement between neighboring acrylamide units and smaller differences in stiffness are observed in the two series of copolymers.

CONCLUSIONS

The addition of NaCl to the aqueous reaction medium results in more random copolymerization of acrylamide with NaAMB. Reactivity ratios determined experimentally at pH 9 changed from $r_1 = 1.23$ and $r_2 = 0.50$ for AM, NaAMB (M_1, M_2) in deionized water to $r_1 = 1.00$ and $r_2 = 0.64$ in NaCl. The change is in accord with screening of electrostatic repulsion between the growing chain and the charged monomer [16, 17]. As a result, 7.1% more NaAMB is incorporated at a 25:75 AM: NaAMB feed ratio.

It was anticipated that reactivity ratio changes might lead to significantly different distributions of monomer sequences and persistence of length changes. Calculations using Igarashi's method show nearly identical NaAMB-centered triad distributions for copolymerizations in deionized or 1 M NaCl solutions. Unfortunately, the calculated distributions only reflect that the mathematical product $r_1 \cdot r_2$ is approximately 0.6 in both cases. This has no apparent physical significance.

Dilute solution behavior of the respective ABAM1 and ABAM2 series as a function of electrolyte concentration reveals significant microstructural differences. Qualitative comparisons of chain stiffness using the Smidsrod-Haug treatment [15] indicate microstructural effects—probably hydrogen-bonding interactions of NaAMB with adjacent AM units—are more effective in maintaining chain dimensions. Such interactions are more effectively attained in synthesis at pH 9 from deionized water than from 1 M NaCl.

Technologically the NaAMB/AM copolymers continue to be of great interest owing to their unusually high viscosity maintenance and phase stability in high-electrolyte and high-temperature environments.

ACKNOWLEDGMENTS

Research support for portions of this work from the Office of Naval Research, the Defense Advanced Research Projects Agency, and the Department of Energy is gratefully acknowledged.

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Received July 29, 1991

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1992	Journal article

4. TITLE AND SUBTITLE
Water-Soluble Copolymers. 43. Ampholytic Copolymers of Sodium 2-Acrylamido-2-Methylpropanesulfonate with 2-Acrylamido-2-Methylpropanetrimethylammonium Chloride

5. FUNDING NUMBERS
C: N00014-89-J-1893

6. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NUMBER
91-92-7

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Avenue
Arlington, VA 22217

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Published in Macromolecules, 1992, 25(7), 1896-1900

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)
See attachment

14. SUBJECT TERMS

15. NUMBER OF PAGES
5

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Unlimited

Water-Soluble Copolymers. 43. Ampholytic Copolymers of Sodium 2-(Acrylamido)-2-methylpropanesulfonate with [2-(Acrylamido)-2-methylpropyl]trimethylammonium Chloride

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Received July 30, 1991; Revised Manuscript Received December 10, 1991

ABSTRACT: Copolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate (NaAMPS) with [2-(acrylamido)-2-methylpropyl]trimethylammonium chloride (AMPTAC) have been prepared by free-radical polymerization in a 0.5 M NaCl aqueous solution using potassium persulfate as the initiator. Copolymer compositions were obtained by ^{13}C NMR and elemental analysis. An r_1r_2 value of 0.31 indicates an alternating microstructure for NaAMPS and AMPTAC monomer units. Molecular weights, second virial coefficients, diffusion coefficients, and average diameters were found using classical and quasielastic low-angle laser light scattering. As the compositions of the copolymers approach equal molar concentrations of NaAMPS and AMPTAC, polyampholyte behavior is observed. The second virial coefficients can be used to distinguish the polyelectrolyte/polyampholyte transition as a function of copolymer composition. The dilute-solution properties of the copolymers, as well as those of the NaAMPS and AMPTAC homopolymers, have been studied as related to composition, pH, temperature, and added electrolytes.

Introduction

Water-soluble copolymers showing tolerance to added electrolytes have been the subject of research in our laboratories in recent years. Of particular interest have been hydrophilic polyampholytes that exhibit enhanced viscosity with added salts.[1-9] Such copolymers containing acidic and basic moieties were reported as early as the 1950s. For example, Alfrey and Morawetz reported the synthesis of vinyl polyampholytes from copolymerization of 2-vinylpyridine and methacrylic acid.[10] These polyampholytes behaved as polyanions in alkaline solution and as polycations in acidic solution. Ehrlich and Doty copolymerized 2-(dimethylamino)ethyl methacrylate with methacrylic acid, varying the composition of the latter from 23 to 57 mol %.[11] The solution and light scattering properties of the copolymer which had 53.7 mol % methacrylic acid were studied at the isoelectric point. The polymer coils possessed negative second virial coefficients A_2, indicating that the hydrodynamic volume of the coils was reduced by intramolecular attractions between the positive and negatively charged groups.

More recently Salamone et al. studied polyampholytes made by pairing anionic and cationic monomers and then polymerizing them into highly alternating copolymers.[12-16] The observed solution behavior was consistent with that of high charge density polyampholytes. We reported polyampholytes containing the cationic monomer [2-(acrylamido)-2-methylpropyl]dimethylammonium hydrochloride (AMPDAC).[3-6] The cationic copolymers at low pH were subject to dehydrochlorination to reduce segmental repulsions, making structure/behavior assessment more difficult. The quaternary cationic monomer [2-(acrylamido)-2-methylpropyl]trimethylammonium chloride (AMPTAC) was synthesized to solve this problem.[8,18] This monomer not only features a quaternized ammonium moiety which remains charged regardless of pH but an amide group which is protected from hydrolysis by geminal methyl groups. This paper reports copolymers of NaAMPS and AMPTAC (Figure 1). In this series the monomers will retain their respective charges over a wide pH range; therefore, the monomer ratio will dictate polymer net charge and the resulting solution properties.

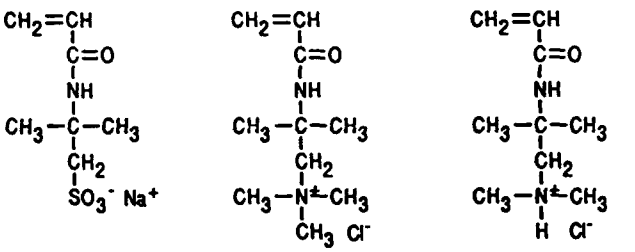

Figure 1. Structures for the monomers sodium 2-(acrylamido)-2-methylpropanesulfonate (NaAMPS), [2-(acrylamido)-2-methylpropyl]trimethylammonium chloride (AMPTAC), and [2-(acrylamido)-2-methylpropyl]dimethylammonium hydrochloride (AMPDAC).

Experimental Section

Materials and Monomer Synthesis. 2-(Acrylamido)-2-methylpropanesulfonic acid (NaAMPS) was obtained from Fluka and purified by recrystallization from a methanol/2-propanol solvent system. Methyl iodide from Aldrich was used without further purification. Synthesis of [2-(acrylamido)-2-methylpropyl]trimethylammonium chloride (AMPTAC) by a multistep procedure has been previously reported.[18] Briefly, [2-(acrylamido)-2-methylpropyl]dimethylamine was reacted with a 10-fold excess of methyl iodide in refluxing diethyl ether and then ion-exchanged to yield the product AMPTAC. Potassium persulfate from J. T. Baker was recrystallized twice from deionized water prior to use.

Synthesis of Copolymers of Sodium 2-(Acrylamido)-2-methylpropanesulfonate with [2-(Acrylamido)-2-methylpropyl]trimethylammonium Chloride. The homopolymers of NaAMPS and AMPTAC and the copolymers of AMPTAC with NaAMPS (the ATAS series) were synthesized by free-radical polymerization in a 0.5 M NaCl aqueous solution under nitrogen at 30 °C using 0.1 mol % potassium persulfate as the initiator. The synthesis and purification procedures have been reported previously.[17,18] The feed ratio of NaAMPS/AMPTAC was varied from 90:10 to 30:70 mol %, with the total monomer concentration held constant at 0.45 M. Aqueous NaCl solutions as the reaction medium ensured that the copolymers remained homogeneous during polymerization.

All copolymers were soluble in deionized water except for ATAS-50. This copolymer precipitated from solution during dialysis and remained insoluble until NaCl was added. This "hydrogel" was washed repeatedly with deionized water to remove

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Table I
Reaction Parameters for the Copolymerization of Sodium 2-(Acrylamido)-2-methylpropanesulfonate (NaAMPS) with [2-(Acrylamido)-2-methylpropyl]trimethylammonium Chloride (AMPTAC)

sample	feed ratio for NaAMPS/AMPTAC	reaction time, h	convn, %	weight % C	weight % N	weight % S	AMPTAC in copolymer, mol % *a*	AMPTAC in copolymer, mol % *b*
ATAS-10-1	90:10	3.3	22.3	31.26	5.79	9.86	14.7 ± 0.4	
ATAS-10-2	90:10	3.8	38.3					21.3 ± 1.3
ATAS-25-1	75:25	1.5	16.2	42.52	7.79	8.38	36.1 ± 1.1	
ATAS-25-2	75:25	3.3	42.0					36.1 ± 2.2
ATAS-40-1	60:40	1.4	28.9	45.55	8.80	7.58	45.4 ± 1.4	
ATAS-40-2	60:40	3.5	34.6					40.0 ± 2.4
ATAS-50-1	50:50	3.3	15.0	46.92	9.37	6.84	51.7 ± 1.6	
ATAS-50-2	50:50	16	61.2					51.0 ± 3.1
ATAS-70-1	30:70	1.5	14.2	47.40	9.81	4.65	65.7 ± 2.0	
ATAS-70-2	30:70	2.5	24.7					62.0 ± 3.7
ATAS-0	100:0	5.8	58.6				0[c]	0[c]
ATAS-100	0:100	5.5	41.2				100[c]	100[c]

[a] Determined from elemental analysis. [b] Determined from ^{13}C NMR. [c] Theoretical.

any remaining salt or monomer and was then lyophilized. Conversions were determined gravimetrically. Table I lists reaction parameters for the copolymerization of AMPTAC with NaAMPS and the homopolymerizations of NaAMPS and AMPTAC. FT-IR (copolymer ATAS-50): 3440 (s, NH) 3296 (s, NH); 3063–2935 (m, CH) 1655 (s, C=O) 1549 (C=O); 1208 cm^{-1} (s, SO). ^{13}C NMR (copolymer ATAS-50): NaAMPS, δ 178.8 (C=O); AMPTAC, δ 178.2 (C=O), 57.8 (quaternary CH_3), 37.8 (chain CH_2), 45.0 (chain CH), 29.4 (gem methyls CH_3).

Copolymer Characterization. Elemental analyses for carbon, hydrogen, nitrogen, and sulfur were conducted by M-H-W Laboratories of Phoenix, AZ, on the low-conversion copolymer samples. Copolymer compositions were confirmed using ^{13}C NMR by integration of the amide carbonyl peaks.[19] ^{13}C NMR spectra were obtained using 10 w/w % aqueous (D_2O) polymer solutions with DSS as the reference. FT-IR spectra were obtained using a Perkin-Elmer 1600 Series FT-IR spectrophotometer. Molecular weight studies were performed on a Chromatix KMX-6 low-angle laser light scattering instrument. Refractive index increments were obtained using a Chromatix KMX-16 laser differential refractometer. For quasielastic light scattering a Langley-Ford Model LF1-64 channel digital correlator was used in conjunction with the KMX-6. All measurements were conducted at 25 °C in 1 M NaCl.

Viscosity Measurement. Stock solutions of sodium chloride (0.10, 0.20, 0.30, 0.50, and 0.75 M NaCl) were prepared by dissolving the appropriate amount of salt in deionized water. Polymer stock solutions were then made by dissolving a specified amount of polymer in solvent from these salt solutions. The solutions were then diluted to required concentrations and allowed to age for 2–3 weeks before being analyzed with a Contraves LS-30 rheometer. Triplicate samples were prepared of each concentration to reduce experimental error. Intrinsic viscosities were evaluated using the Huggins equation.[20]

Results and Discussion

The ATAS series of copolymers was synthesized by varying the ratio of NaAMPS and AMPTAC from 90:10 to 30:70 mol % in the feed. Reaction parameters and the resulting copolymer compositions determined by elemental analysis or ^{13}C NMR are given in Table I. The number appended to the acronym ATAS refers to the amount of AMPTAC in the feed. This series differs from the previously studied ADAS series[3,4] in which AMPDAC was the cationic monomer. The quaternary ammonium group of AMPTAC has been shown to be a stable cationic moiety which remains charged over a wide pH range.[18] When AMPDAC was used in the ADAS copolymers, the exact number of cations present was never precisely known due to loss of HCl from the tertiary amine hydrochloride in aqueous solution. The AMPTAC monomer and ATAS copolymers have no facile route for charge elimination other than counterion condensation, making them better suited for structure/property studies.

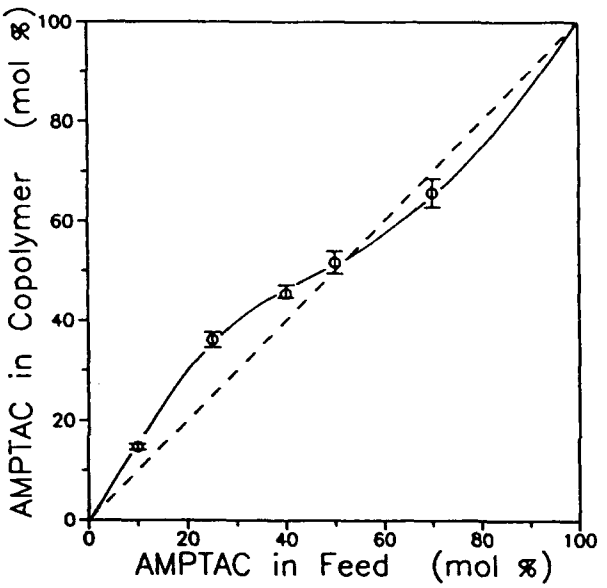

Figure 2. Mole percent AMPTAC incorporated into the ATAS copolymers as a function of the comonomer feed ratio. The dashed line represents an ideal random incorporation.

Compositional Studies. Elemental analysis was used to determine the copolymer compositions from nitrogen and sulfur content represented by eqs 1 and 2. The

$$\%\ N/14.01 = A + 2B \quad (1)$$

$$\%\ S/32.06 = A \quad (2)$$

coefficients A and B are the number of moles of NaAMPS and AMPTAC, respectively, in a normalized amount of copolymer, e.g., 1 g. The mole percent of each monomer in the copolymer may then be determined using eq 3 and 4.

$$\text{mol \% NaAMPS} = A/(A + B) \times 100\% \quad (3)$$

$$\text{mol \% AMPTAC} = B/(A + B) \times 100\% \quad (4)$$

Integration of ^{13}C NMR amide carbonyl peaks also gave the mole percent of NaAMPS and AMPTAC in the copolymers. This information agrees favorably with that derived from elemental analysis. The low- and high-conversion data differ significantly only for ATAS-10 in which compositional drift would be expected for an alternating copolymerization as indicated by the values of r_1 and r_2. The copolymer compositions as a function of feed composition are shown in Figure 2. A copolymeri-

Table II
Reactivity Ratios for the ATAS and ADAS Copolymer Series Determined Using the Methods of Kelen-Tüdős and Fineman-Ross

	ATAS			ADAS		
method	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2
Kelen-Tüdős	0.50 ± 0.02	0.62 ± 0.02	0.31	0.22 ± 0.02	0.31 ± 0.04	0.07
Fineman-Ross	0.58 ± 0.06	0.87 ± 0.09	0.50	0.22 ± 0.03	0.33 ± 0.05	0.07

Table III
Structural Data for the Copolymers of Sodium 2-(Acrylamido)-2-methylpropanesulfonate (NaAMPS, M_1) with [2-(Acrylamido)-2-methylpropyl]trimethylammonium Chloride (AMPTAC, M_2)

	AMPTAC in copolymer,[a]	blockiness, mol %		alternation for M_1-M_2,	mean sequence length	
sample	mol %	M_1-M_1	M_2-M_2	mol %	M_1	M_2
ATAS-10	14.7	71.4	0.8	30.5	5.5	1.1
ATAS-25	36.1	35.1	7.3	54.0	2.5	1.2
ATAS-40	45.4	22.9	13.6	63.2	1.8	1.4
ATAS-50	51.7	16.3	19.6	64.1	1.5	1.6
ATAS-70	65.7	6.4	37.8	54.5	1.2	2.5

[a] Determined from elemental analysis.

zation in which an ideally random copolymer would be formed is represented by the dashed line.

Reactivity Ratio and Microstructure Studies. Reactivity ratios for the ATAS series were determined from the feed ratios of the monomers and the resultant copolymer compositions obtained by elemental analysis. The traditional methods of Fineman-Ross[21] and Kelen-Tüdős[22] were employed to determine the monomer reactivity ratios from the low-conversion copolymer samples. The Fineman-Ross method gave reactivity ratios of NaAMPS (M_1) and AMPTAC (M_2) of $r_1 = 0.58$ and $r_2 = 0.87$. The Kelen-Tüdős method produced reactivity ratios of 0.50 and 0.62 r_1 and r_2, respectively, and $r_1r_2 = 0.31$ (Table II). The copolymer compositions as a function of feed composition for the ATAS series are shown in Figure 2. The experimental data suggest the ATAS copolymers, like the previously reported series ADAS, are highly alternating.

Microstructural information was obtained statistically using the equations of Igarashi[23] and Pyun[24] and is presented in Table III. The Igarashi method calculates the fractions of NaAMPS-NaAMPS, AMPTAC-AMPTAC, and NaAMPS-AMPTAC units in the copolymers as a function of reactivity ratios and copolymer compositions. The Pyun method calculates the mean sequence length of the monomers in each copolymer. The data clearly indicate the alternating tendency of the monomer sequences. The ATAS copolymers, however, do not possess the degrees of alternation obtained for the ADAS copolymers. For example, ADAS-50 had a 15 mol % higher alternation value than the analogous ATAS-50. This is indicative of NaAMPS/AMPDAC having a stronger interaction than the NaAMPS/AMPTAC ion pair.

Light Scattering Studies. Classical and quasielastic light scattering data for the ATAS series are presented in Table IV. The polymers have molecular weights from 1.47×10^6 for the ATAS-100 homopolymer to 7.92×10^6 for ATAS-40-2. The second virial coefficients (A_2) were found to exhibit dependence on copolymer composition. ATAS-50-2 with a 50:50 mol % charge composition is better solvated in the presence of electrolytes than the copolymers with charge imbalances. ATAS-25-2 has a negative A_2 value while ATAS-50-2 has an A_2 value of 0.763×10^{-4} mL·mol/g^2. Similar results had been observed for the ADAS copolymers in which ADAS-50 had the highest A_2 value for the series. The data are consistent with the expected polyelectrolyte/polyampholyte transitions depending on the extent of AMPTAC incorporation in the copolymers. Higgs and Joanny have presented theoretical predictions which agree with our results.[25]

The narrow distributions of experimental values for the diffusion coefficients (D_0) and average hydrodynamic diameters (d_0) are consistent with the viscosity behavior of the copolymers in electrolyte solutions. In 1 M NaCl, the ATAS copolymers are neither chain extended nor chain constricted due to charge screening. In deionized water, large differences would be expected for polyampholytes, i.e., ATAS-50-2, and polyelectrolytes, i.e., ATAS-10-2 and ATAS-70-2 (Table IV), where strong electrostatic effects would dominate. Experimental difficulties, unfortunately, preclude meaningful light scattering studies of the high charge density polyampholytes in deionized water. Viscometric studies, however, support the above discussion.

Viscometric Studies. The dilute-solution behavior of the ATAS series was studied with respect to composition, temperature, pH, and added electrolytes. Apparent viscosities of the polymers were measured at polymer concentrations below C^* using a Contraves LS-30 low-shear rheometer. The solutions were aged 2–3 weeks to allow equilibration of polymer conformations in solution. Intrinsic viscosities were calculated using the Huggins relationship.

The solution behavior of the homopolymer ATAS-100 was previously examined in the pH range of 3–11 in 0.1 M NaCl.[17] No dependence of the apparent viscosity was observed. Each copolymer of AMPTAC with the sulfonate monomer NaAMPS should be nondependent on changes in pH above 3 since the sulfonate group remains ionized.

Intrinsic viscosities for the copolymers ATAS-50 and -70 and the homopolymer ATAS-100 are relatively independent of temperature when measured in deionized water and in 0.5 M NaCl in the temperature range of 25–60 °C. Most polyelectrolytes exhibit reductions in viscosity as a function of increasing temperature due to the elimination of rotational restrictions. Increases in conformational freedom may be offset by water restructuring around the NaAMPS and AMPTAC ion pairs.

Effects of Copolymer Composition. The apparent viscosities of the ATAS copolymers in deionized water plotted as a function of composition are shown in Figure 3. A decrease in the apparent viscosity develops as the molar ratio of NaAMPS and AMPTAC approaches unity. The curve is discontinuous due to the insolubility of ATAS-50-2 in the absence of added electrolytes. This is the result of decreasing polymer hydrodynamic volume caused by increasing intramolecular associations. The ADAS copolymers displayed a similar effect.[3,4]

The effects of composition on the intrinsic viscosity in NaCl solutions are displayed in Figure 4. The homopolymer ATAS-0 and the copolymers ATAS-10-2, -25-2, -40-2, and -50-2 have comparable molecular weights which lead to similar viscosities in 0.75 M NaCl. In 0.1 M NaCl, the polyelectrolyte effect dominates solution viscosity and significant differences due to composition can be discerned. Copolymers with more NaAMPS than AMPTAC act as

Table IV
Classical and Quasielastic Light Scattering Data for Copolymers of Sodium 2-(Acrylamido)-2-methylpropanesulfonate (NaAMPS) with [2-(Acrylamido)-2-methylpropyl]trimethylammonium Chloride (AMPTAC)

sample	AMPTAC in copolymer,[a] mol %	dn/dc	$M_w \times 10^{-6}$	$A_2 \times 10^4$, mL·mol/g^2	$D_0 \times 10^8$, cm^2/g	d_0, Å	DP $\times 10^{-4}$
ATAS-0	0.0	0.1116	6.12	0.92	3.87	1270	2.23
ATAS-10-2	14.7	0.1190	8.22	0.49	4.19	1300	2.67
ATAS-25-2	36.1	0.1229	6.20	−0.02	4.73	1050	3.61
ATAS-40-2	45.4	0.1405	7.92	0.59	3.85	1290	2.75
ATAS-50-2	51.7	0.1445	7.68	0.76	4.63	1000	3.52
ATAS-70-2	65.7	0.1454	4.98	0.34	4.06	1250	3.42
ATAS-100	100.0	0.1458	1.47	2.11	6.37	920	0.67

[a] Determined from elemental analysis.

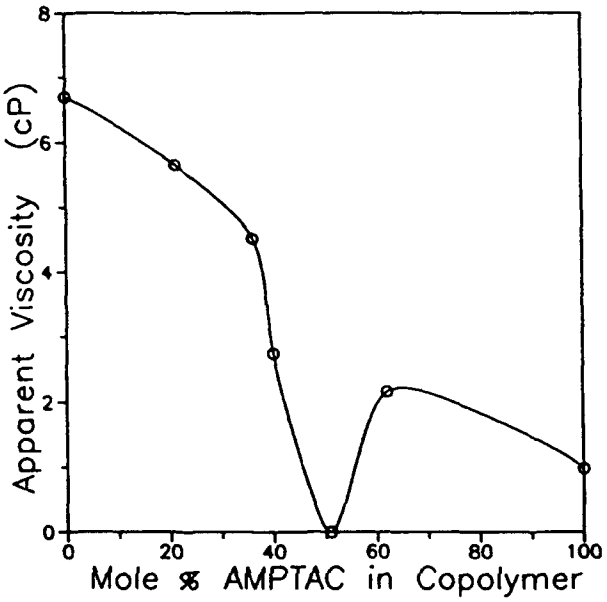

Figure 3. Effect of copolymer composition on the apparent viscosity of 0.025 g/dL ATAS polymer solutions in deionized water at 25 °C at a shear rate of 5.96 s^{-1}.

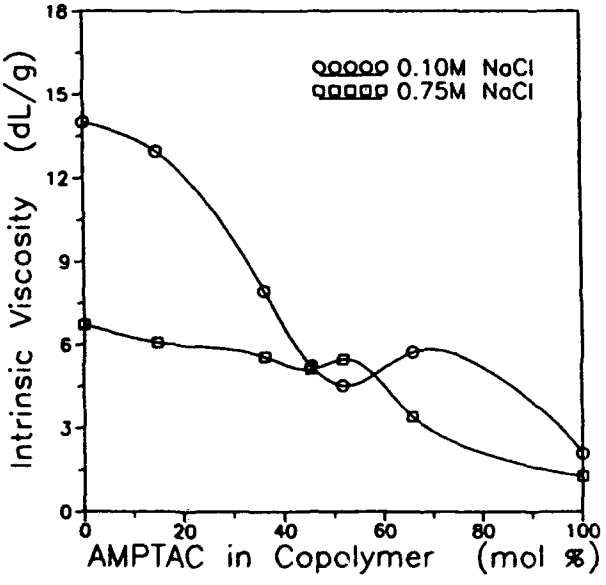

Figure 4. Intrinsic viscosity of the ATAS copolymer series as a function of the composition in 0.10 and 0.75 M NaCl determined at a shear rate of 5.96 s^{-1} at 25 °C.

polyanions. As the amount of AMPTAC in the copolymers increases to 50 mol %, the viscosity decreases as a result of increasing polyampholyte character. This behavior agrees with the second virial coefficient data. The copolymer ATAS-70-2 which has 65.7 mol % AMPTAC and the homopolymer ATAS-100 have low intrinsic

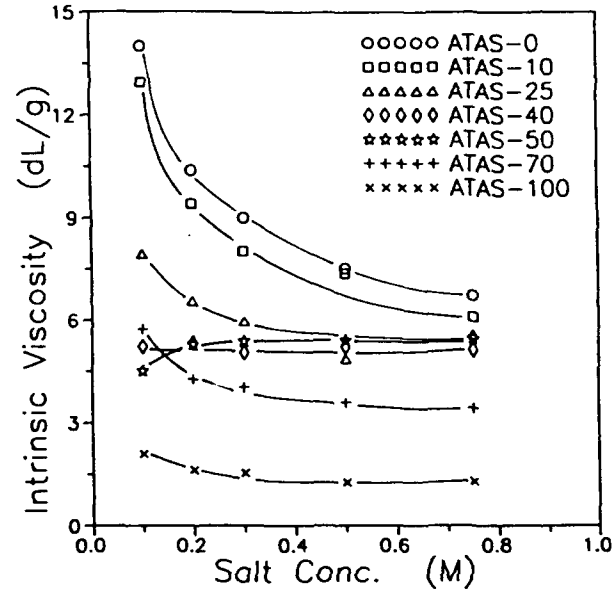

Figure 5. Intrinsic viscosities for the ATAS copolymers as a function of NaCl concentration determined at a shear rate of 5.96 s^{-1}.

viscosities due to polycationic character. The intrinsic viscosity of ATAS-50-2, which is insoluble in deionized water, increases with increasing ionic strength.

Effects of Added Electrolytes. The effects of sodium chloride on the intrinsic viscosities of the ATAS copolymers and ATAS-0 and ATAS-100 were determined at a shear rate of 5.96 s^{-1} at 25 °C (Figure 5). ATAS-0, the anionic homopolymer of NaAMPS, shows the greatest decrease in viscosity as the NaCl concentration increases. As more AMPTAC is incorporated into the copolymer, this effect becomes less pronounced due to the transition from polyelectrolyte to polyampholyte character. ATAS-40-2 lies near the polyampholyte composition region but still possesses a net charge. This leads to a small change in viscosity for ATAS-40-2 with increasing ionic strength. At equal molar concentrations of each monomer (ATAS-50-2), there is an increase in the viscosity. The copolymer ATAS-70-2 lies on the edge of the polyelectrolyte/polyampholyte transition and thus shows a small decrease in the intrinsic viscosity.

The intrinsic viscosity of each sample was plotted as a function of the inverse square root of the ionic strength (Figure 6). Polyelectrolytes show a direct linear dependence when plotted in this manner.[26] The polymers ATAS-0, -10-2, and -100 exhibit linear behavior and positive slopes. The copolymers ATAS-50-2 and -40-2 exhibit slightly negative slopes indicative of polyampholyte nature and consistent with the second virial coefficient data. Intermediate behavior is observed for ATAS-25-2 and ATAS-70-2.

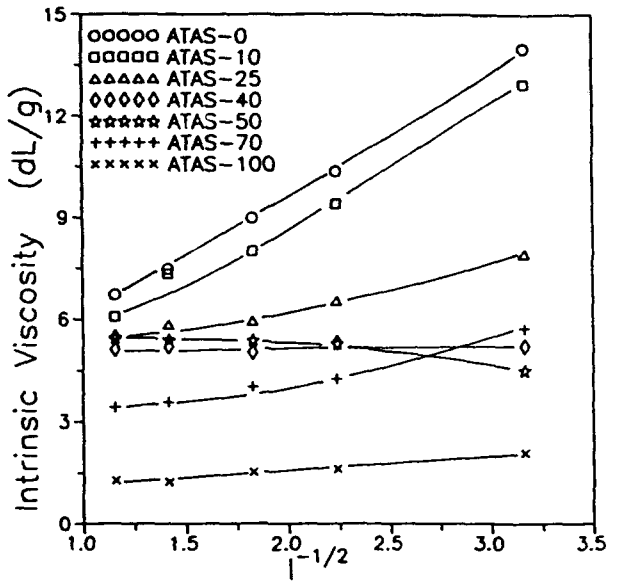

Figure 6. Intrinsic viscosities for the ATAS copolymers as a function of the inverse square root of the ionic strength.

Conclusions

Homopolymers of NaAMPS and AMPTAC and the copolymers of NaAMPS with AMPTAC (the ATAS series) have been synthesized by free-radical polymerization in 0.5 M NaCl. The presence of NaCl allows the polymerizations to remain homogeneous, yielding copolymers with microstructures less alternating than those of the previously studied ADAS series. Copolymer compositions were obtained by elemental analysis and ^{13}C NMR. Reactivity ratios determined by the methods of Fineman–Ross and Kelen–Tüdõs yield $r_1r_2 \approx 0.31$. Molecular weights range from 1.47 to 7.92 × 10^6 for the AMPTAC homopolymer and the ATAS-40 copolymer, respectively. Second virial coefficients indicate a copolymer with an equal molar concentration of each monomer to be better solvated than copolymers with charge imbalances. Second virial coefficients and ionic strength changes may be used to detect polyampholyte/polyelectrolyte transitions with compositional changes. ATAS-0, -10, -25, -75, and -100 behave as polyelectrolytes, while ATAS-40 and -50 show polyampholyte behavior.

In the absence of added electrolytes, decreasing viscosities are observed as copolymer compositions approach equal molar values. This is attributed to decreasing polymer hydrodynamic volumes caused by increasing intramolecular associations. In 1 M NaCl the copolymers are neither chain extended nor chain constricted due to charge screening by the added electrolytes. The use of the quaternary ammonium monomer AMPTAC allows the synthesis of high charge density polyelectrolytes and polyampholytes with precisely known charge ratios, thus allowing accurate assessment of structure/property relationships.

Acknowledgment is due to Kent Newman for the ^{13}C NMR work, Kelly Anderson for helping with the viscometric studies, and the Department of Energy, the Office of Naval Research, and the Defense Advanced Research Projects Agency for support of this research.

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Registry No. NaAMPS, 5165-97-9; NaAMPS (homopolymer), 35041-59-9; AMPTAC, 51730-62-2; AMPTAC (homopolymer), 51730-63-3; (NaAMPS)(AMPTAC) (copolymer), 139101-46-5.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1992	Preprint

4. TITLE AND SUBTITLE
Hydrophobically Associating Water Soluble Copolymers for the Study of Drag Reduction

5. FUNDING NUMBERS
C: N00014-89-J-1893

6. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NUMBER
91-92-8

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Avenue
Arlington, VA 22217

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Published in ANTEC Conference Proceedings, 1992, 38, 2095-2099

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*
See attachment

14. SUBJECT TERMS

15. NUMBER OF PAGES
5

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Unlimited

Hydrophobically Associating Water Soluble Copolymers for the Study of Drag Reduction

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INTRODUCTION

Frictional resistance in turbulent flow can be reduced to as little as one-quarter that of the pure solvent by the addition of extremely small concentrations of soluble polymers. This drag reduction phenomenon shown by polymeric additives has been known since 1949, when it was first reported by B.A.Toms [1]. There has been considerable research in this area over the last three decades but there is no universally accepted model that explains the mechanism by which macromolecules act to bring about frictional reduction. Some quantitative models have accurately predicted drag reduction behavior of water-soluble homopolymers like poly(ethylene oxide) and polyacrylamide. Recently our research group has undertaken extensive analyses of polymers of widely differing structures and compositions [2,3,4].

Most of the theories for drag reduction are interrelated and include variations of the idea that polymer molecules somehow interact with vortices that are formed in turbulent flow and dissipate energy necessary for the vortices to grow. This energy may be dissipated through breakage of primary or secondary bonds, conformational changes, associations/dissociations, by inducing changes in the solvent structure around the macromolecules, or by some other mechanism. Many theories also include the concept that the polymer molecules act near the wall in the boundary layer.

Molecular parameters in drag reduction:

The molecular parameters which affect drag reduction are molecular weight, molecular weight distribution, chemical nature of the polymer (e.g. ionic or non-ionic), branching and copolymer composition, solvent quality, critical concentration, second virial coefficient, hydrodynamic volume, entanglements and energetic interactions (association, aggregation, and hydrogen bonds).

Polymer chain flexibility improves drag reduction for a large number of polymers because of better interaction with the turbulent eddies. Linear polymers have been found to be more effective than branched samples, which is expected since branching leads to less flexibility. However, these conclusions do not hold for all polymer systems.

Previous studies in our research group:

Four series of high molecular weight, water soluble acrylamide copolymers with systematic variations in structure and chemical composition were synthesized and thoroughly characterized. The comonomers used with acrylamide are shown in Figure 1. They are sodium acrylate (NaA), sodium 2-acrylamido-2-methylpropane sulfonate (NaAMPS), sodium 3-acrylamido-3-methyl butanoate (NaAMB), and diacetone acrylamide (DAAM). All copolymers were found to conform to a universal curve when normalized for hydrodynamic volume fraction of polymer in solution as shown in Figure 2 [2,3,5]. The number following an acronym denotes the mole percent of that comonomer (the rest being acrylamide) in the feed to produce a given copolymer.

The most efficient drag reducers are the polymers that yield the greatest values of (%DR/[η]C), the percent drag reduction per unit volume fraction, at the lowest volume fractions. Of the polymers we have investigated thus far, the hydrophobically associating DAAM copolymers are the most efficient. The uncharged homopolymers, polyacrylamide (PAM) and poly(ethylene oxide) (PEO), yield moderate values and the homopolyelectrolytes are the least efficient. These results also prove that polymer associations and solvation play an important role in the drag reduction phenomenon.

As mentioned above, copolymers having some degree of hydrophobic inter- and intramolecular interactions have proven to be the most efficient drag reducers relative to the other polymers and copolymers that have been studied in our laboratory. Therefore, a new series of hydrophobically associating copolymers, poly(acrylamide-co-N-isopropylacrylamide) (AM-Co-IPAM), has been synthesized and characterized. The aqueous solution properties of these copolymers are extremely sensitive to sodium chloride, urea and sodium dodecyl sulfate (SDS) concentration and temperature. Thus, these polymers are good models to assess the effect of solvation on drag reduction performance.

EXPERIMENTAL

Materials: Acrylamide (Aldrich, 97%) was recrystallized three times from acetone. N-isopropylacrylamide (Eastman Kodak Chemical) was recrystallized twice from ethyl acetate. Sodium chloride (Fisher Chemical), urea (Aldrich, 99+%) and sodium dodecyl sulfate (Sigma, 99%) were used as received.

Methods: Polymer Synthesis. Polymerizations were performed in aqueous solution using 0.2 mole% potassium persulfate free radical initiator at 30°C under a nitrogen atmosphere (Figure 3). Total monomer concentration was 0.45 M. The reactions were terminated by the addition of catechol after approximately 4.5 hours of polymerization time. Polymer conversions of 50% to 60% were obtained. Copolymers were purified by dialysis. The dialyzed copolymer solutions were freeze dried.

Polymer Characterization. ^{13}C NMR (JEOL FX90Q, Carbon 22.5 MHz) and elemental analysis (M-H-W Laboratories, Phoenix, AZ) were used to determine copolymer compositions. The calorimetric data were obtained on a Microcal, Inc., Model MC-1 microcalorimeter. Polymer free solutions of the same composition were used in the reference cell. The viscometric studies were performed on a Cannon-Ubbelohde four-bulb shear dilution viscometer. Low angle laser light scattering was performed on a Chromatix KMX-6 spectrophotometer utilizing a 2mW He-Ne laser operating at 633 nm. The dn/dc measurements were obtained on a Chromatix KMX-16 laser differential refractometer.

Drag Reduction Measurements: The drag reduction measurements were performed on a capillary flow apparatus and on a modified rotating disk rheometer. The capillary flow apparatus consists of a high pressure nitrogen gas source that can drive up to 1000 ml of fluid through a 0.210 cm X 102 cm capillary. The capillary pressure drop and flow rate can be obtained from this apparatus and these parameters are used to calculate the Reynolds numbers (Re) and the fluid friction factors (f). The rotating disk rheometer consists of a

circular disk rotating in a cylindrical chamber. The Reynolds numbers and fluid friction factors can be obtained by monitoring torque against rpm values. The two instruments are different in that, in the capillary flow the entire solution is in turbulence whereas in the rotating disk rheometer only the solution close to the outer edge of the disk is in turbulence. In the latter, the polymer molecules can go in and out of turbulence. The percent drag reduction (%DR) can be determined from the knowledge of the solvent (f_s) and solution (f_p) friction factors at a particular Reynolds number or wall shear stress.

$$\%DR = 100 \times (f_s - f_p) / f_s \qquad (1)$$

RESULTS AND DISCUSSION

The amount of N-isopropylacrylamide (IPAM) monomer in the feed was varied from 100, 85, 70, 55 to 40 mole percent. The reactivity ratios (Table I) were calculated from the feed ratios of the monomers and the copolymer compositions, at low conversion (~ 10%), using the Kelen-Tudos [6] and the Fineman-Ross [7] techniques. The reactivity ratios indicate random copolymerization.

The solution properties of these copolymers were studied in deionized water, 0.514 M NaCl and 1 M urea solutions. In 0.514 M NaCl the hydrophobic associations are enhanced due to water structuring in presence of the ions. In 1 M urea the water structuring is diminished due to the breaking of the extensive hydrogen bonding present in deionized water.

All the copolymers with the exception of IPAM-40 show lower critical solution temperatures (LCST) or cloud points below 100°C. The cloud points in deionized water for IPAM-100, IPAM-85, IPAM-70 and IPAM-55 are 34°C, 42°C, 53°C and 74°C respectively. As expected, with the addition of acrylamide to the copolymers the cloud points are raised and the copolymers become more hydrophilic. The cloud points are lowered in 0.514 M NaCl. Thus, the solubility of these copolymers is reduced in the presence of NaCl.

Since these copolymers precipitate on heating, they are well suited for microcalorimetric studies. The microcalorimetric studies were performed at a scanning rate of 30°C/hr. Figure 4 shows the microcalorimetric endotherms for IPAM-100 in different solvents. The endotherm for IPAM-100 in deionized water is sharper than those previously reported [8]. This apparently is a molecular weight (MW) effect as the MW of our polymer is an order of magnitude higher than the highest MW sample reported in Reference 8.

Table II summarizes the microcalorimetric properties of IPAM-100 in different solvents. ΔH and ΔS increase with the addition of NaCl. The higher ΔS indicates that NaCl is a water-structure maker (kosmotrope). The cloud point decreases in the presence of NaCl. The cloud points and the microcalorimetric T_{max} concur fairly well. The enthalpy of IPAM-100 in deionized water is consistent with the loss of approximately 1 hydrogen bond/repeat unit as reported by Fujishige et al [9]. ΔH and ΔS decrease on the addition of urea. The lower ΔS indicates that urea is a water-structure breaker (chaotrope). There is an enthalpy-entropy compensation in all cases. The cloud point decreases in the presence of urea. This occurs for IPAM-85 as well but the trend reverses for IPAM-70 and IPAM-55. The depression of the cloud point in IPAM-100 and IPAM-85 in urea is unexpected. The microcalorimetric endotherms are very sharp for IPAM-100 in deionized water and NaCl solutions ($\Delta T_{1/2} < 0.5$°C) but the endotherms broaden with the addition of urea. The calorimetric peak is higher ($\Delta C_p > 35$) in deionized water and NaCl but it drops drastically in the presence of urea and the decrease is proportional to the urea concentration.

The endotherms become broader ($\Delta T_{1/2} > 2.5$°C) on the introduction of acrylamide into the copolymers. The ΔH is directly related to the amount of N-isopropylacrylamide in the copolymer. There is an extreme drop in the peak height (ΔC_p) with the addition of acrylamide to the copolymers.

The viscometric studies were conducted as a function of solvent and temperature. The viscosities of all these copolymers conform to the Huggins and the Kraemer equations. Extrapolations to a common intercept at zero concentration from plots of reduced viscosity (η_{sp}/C) and inherent viscosity ($ln\eta_r/C$) versus concentration (C) were used to determine intrinsic viscosities ($[\eta]$). The zero-shear intrinsic viscosities are reported in Table III. The viscosities are lower in NaCl relative to those in deionized water due to enhanced intramolecular hydrophobic associations. In urea the hydrodynamic volume is lower due to diminished hydrogen bonding leading to less solvent being bound to the polymer. Therefore, the solution properties of these copolymers are influenced by a subtle interplay of hydrophobic associations and hydrogen bonding.

Temperature has a drastic effect on intrinsic viscosity. As the temperature approaches the LCST, the copolymer exhibits a lower hydrodynamic volume as shown for IPAM-100 and IPAM-85 in Table III. The lowering of intrinsic viscosity at higher temperature was noted by Heskins and Guillet [10] who observed that poly(N-isopropylacrylamide) tends to aggregate as the temperature approaches the LCST.

In 0.2% (~ 7mM) sodium dodecyl sulfate (SDS), the alkyl chain of the surfactant molecules associates with the polymer backbone. Consequently, very high intrinsic viscosities are realized due to the charge-charge repulsion between adjacent surfactant molecules and the disruption of intramolecular hydrophobic associations. These intrinsic viscosities in SDS are very shear rate dependent, showing a highly shear-thinning response.

Tables IV summarizes the classical light scattering results of IPAM copolymers in deionized water. The dn/dc (change in refractive index with concentration) values vary between 0.190 and 0.230 for all the copolymers. The weight average molecular weights (M_w) are between 3.0 and 5.2 million g/mole. The weight average degree of polymerization (DP_w) is relatively low for IPAM-100, IPAM-85 and IPAM-40 and is relatively high for the homopolymer of acrylamide (PAM). The second virial coefficients (A_2), which are related to the solubility of the polymer in the solvent, increase from IPAM-100 to PAM. Thus, IPAM-100 which is the most hydrophobic is the least soluble, and PAM which is the most hydrophilic is the most soluble in deionized water.

The drag reduction studies were conducted in deionized water, 0.514 M NaCl, 1 M urea and 0.2% SDS. Figure 5 depicts the drag reduction profiles for IPAM-40 in different solvents on the rotating disk rheometer. The percent drag reduction (%DR) is higher in deionized water relative to that in salt and urea. In 0.514 M NaCl the intramacromolecular hydrophobic associations are enhanced, leading to the lowest %DR. In 1 M urea the breaking of the water structure leads to less water being associated with the polymer coil leading to lower %DR. These results are supported by the microcalorimetric, the turbidimetric as well as the viscometric studies. On the rotating disk rheometer, the drag reduction profiles for all the copolymers are similar to those shown for IPAM-40 (Figure 5). The homopolymer of acrylamide however, shows almost the same %DR in all three solvents.

In Figure 6, the drag reduction profiles of IPAM-70 are depicted in 0.2% (~ 7mM) SDS, 0.514 M NaCl and 1 M urea in capillary flow. IPAM-70 and all the other copolymers show the highest %DR in 0.2% SDS relative to the other solvents. In SDS, the solvation changes within or around the massive hydrodynamic domains may be more effective in interacting with vortices that are formed in turbulent flow. Also, the surfactant molecules, that are in a dynamic association/dissociation equilibrium, provide another mechanism for dissipating the energy in turbulence. The %DR in deionized water, not shown in Figure 6, is slightly below that in 0.2% SDS and is higher than that in salt and urea. The %DR in 0.514 M NaCl is the lowest and that in urea shows an intermediate value due to the reasons presented in the previous paragraph. In capillary flow the drag reduction profiles of IPAM-100 and IPAM-85 are similar to those for IPAM-70.

Figure 7 shows the drag reduction profiles for IPAM-40 in different solvents in capillary flow. Like the other copolymers, IPAM-40 shows the highest %DR in 0.2% SDS. For IPAM-40 in capillary flow, the %DR in 1 M urea is the lowest with 0.514 M NaCl solutions showing intermediate values. Since IPAM-40 does not have as many N-isopropylacrylamide moieties on the polymer chain as compared to the other copolymers, it forms weaker intramolecular hydrophobic associations. These associations are enhanced in 0.514 M NaCl, but under high shear conditions in capillary flow, where the polymer cannot go in and out of the turbulent regime, part of these associations are broken resulting in a slightly higher %DR. At a wall shear stress of 143 Pa, the 0.514 M NaCl curve falls almost on top of the 0.2% SDS curve. In urea, the breaking of the water structure leads to a lesser amount of solvent being associated with the polymer chain, resulting in lower %DR values. Therefore, for IPAM-40 in capillary flow, the breaking of the water structure in urea leads to the lowest %DR. The intramolecular hydrophobic associations become less significant. IPAM-55 shows the intermediate situation between IPAM-70 and IPAM-40 where the %DR in urea is almost the same as that in salt and the %DR in 0.2% SDS is higher.

Figure 8a shows the IPAM copolymers plotted in the universal curve format. The polymers showing the highest %DR per unit volume fraction, at the lowest volume fractions are the most efficient drag reducers. IPAM-70 and IPAM-55 are more efficient drag reducers than PAM whereas IPAM-100 and IPAM-40 are less efficient drag reducers than PAM in deionized water. On plotting DR efficiency versus IPAM content in the copolymer (Figure 8b), it is seen that the most efficient drag reducers are neither the most hydrophobic copolymers or the most hydrophilic copolymers, they fall somewhere in between the two extremes. From the IPAM copolymers the most efficient drag reducer is IPAM-70.

CONCLUSIONS

Poly (acrylamide-co-N-isopropylacrylamide) copolymers have been synthesized and characterized by elemental analysis, ^{13}C NMR, turbidimetry, microcalorimetry, viscometry and light scattering. The dilute solution and drag reduction properties of the copolymers are explained on the basis of intramolecular hydrophobic associations and hydrogen bonding and its effect on water structure. Copolymers with intermediate hydrophobicity are found to be

the most efficient drag reducers. IPAM-70 was the most efficient drag reducer from this copolymer series.

ACKNOWLEDGEMENTS

We are grateful to Professor David A. Tirrell (University of Massachusetts) and his research group for allowing us the use of their microcalorimeter. Financial support from the Office of Naval Research, the Defence Advanced Research Projects Agency, and the Department of Energy is also gratefully acknowledged.

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Table I: Reactivity ratios

Method	r_1	r_2	$r_1 r_2$
Kelen-Tudos	0.95	1.04	0.99
Fineman-Ross	0.98	1.06	1.04

Monomer 1 = Acrylamide (AM).
Monomer 2 = N-isopropylacrylamide (IPAM).

Table II: Microcalorimetric properties of IPAM-100 (0.04 g/dL) in different solvents

Solvent	T_{max}[a] (°C)	$\Delta T_{1/2}$[b] (°C)	ΔH[c]	ΔS[d] (cal.°C^{-1}.mole^{-1})	ΔC_p[e] (cal.°C^{-1}.g^{-1})
DI water	34.0	0.4	18.2 (2.1)	6.7	37
0.25 M NaCl	30.6	0.4	18.7 (2.1)	7.0	39
0.514 M NaCl	27.2	0.4	19.6 (2.2)	7.4	39
1 M Urea	33.2	0.5	11.9 (1.3)	4.4	26
2 M Urea	32.2	0.6	11.0 (1.2)	4.1	22
4 M Urea	29.4	1.1	8.5 (1.0)	3.2	9

[a] Temperature of the peak of the microcalorimetric endotherm. [b] The width at half height of the microcalorimetric endotherm. [c] Enthalpy of endotherm in cal/g of polymer. The values in parantheses are kcal/mole of monomer repeat units.
[d] Entropy of endotherm calculated from $\Delta H = T\Delta S$ at the LCST when $\Delta G = 0$.
[e] Calorimetric peak height.

Table III: Zero-shear intrinsic viscosities (dL/g) in different solvents at 30°C

Sample	DI water	0.514 M NaCl	1 M Urea	0.2% SDS
IPAM-100	4.7	–[a]	3.4	20.1
	8.2 (at 20°C)			
IPAM-85	7.3	5.1	5.7	20.9
	2.7 (at 40°C)			
IPAM-70	6.4	5.3	5.2	27.9
IPAM-55	9.7	9.3	7.0	31.8
IPAM-40	8.2	7.9	9.2	27.4
PAM	22.3	15.6	16.3	14.0

[a] Cloud point occurs at 27.5°C.

Table IV: Light scattering data of IPAM copolymers in DI water

Sample	dn/dc	$M_w \times 10^{-6}$ (g.mole^{-1})	$A_2 \times 10^4$ (ml.mole.g^{-2})	$DP_w \times 10^{-4}$
IPAM-100	0.2079	3.0	2.94	2.65
IPAM-85	0.1995	3.1	3.01	2.90
IPAM-70	0.1970	4.5	3.31	4.44
IPAM-55	0.1927	3.9	3.46	4.13
IPAM-40	0.2247	2.2	3.62	2.49
PAM	0.2167	5.2	3.78	7.31

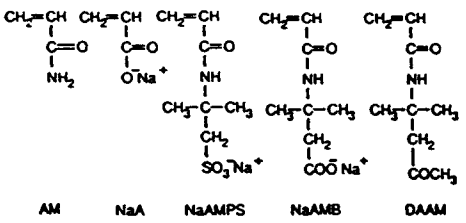

Figure 1

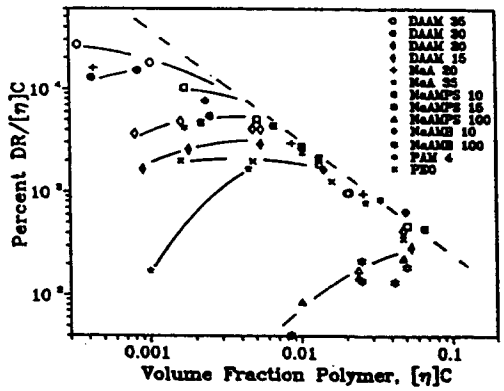

Figure 2: Percent DR per unit volume fraction versus volume fraction in 0.514 M NaCl on a rotating disk rheometer, Re = 520,000 [2].

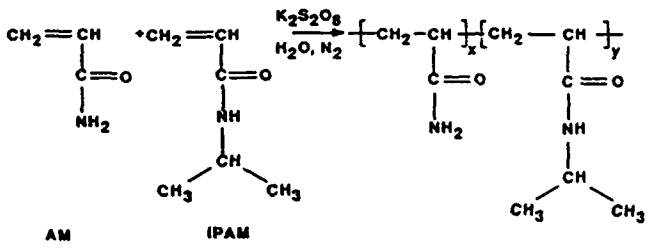

Figure 3: Polymer Synthesis

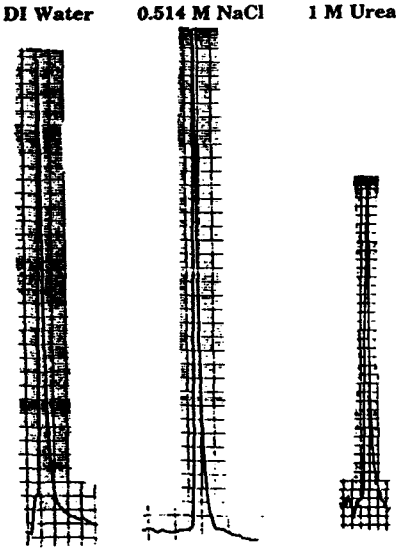

Figure 4: Microcalorimetric endotherms for IPAM-100 (0.04 g/dL) in different solvents.

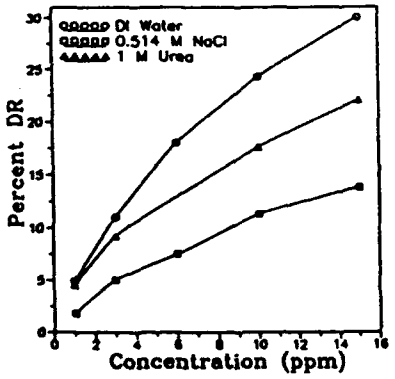

Figure 5: Percent DR versus concentration for IPAM-40 in different solvents at T_w = 112 Pa on the rotating disk rheometer.

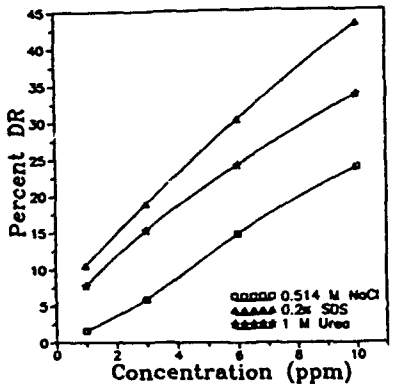

Figure 6: Percent DR versus concentration for IPAM-70 in different solvents at T_w = 36 Pa in the capillary flow apparatus.

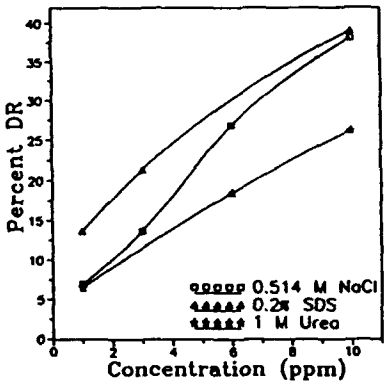

Figure 7: Percent DR versus concentration for IPAM-40 in different solvents at T_w = 36 Pa in the capillary flow apparatus.

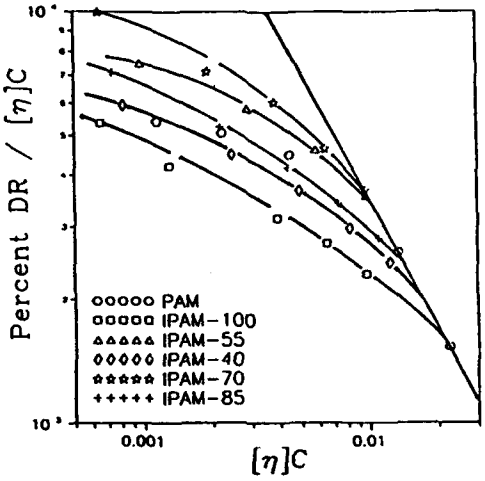

Figure 8a: Percent DR per unit volume fraction versus volume fraction in deionized water on a rotating disk rheometer, T_w = 112 Pa (Re = 848,500).

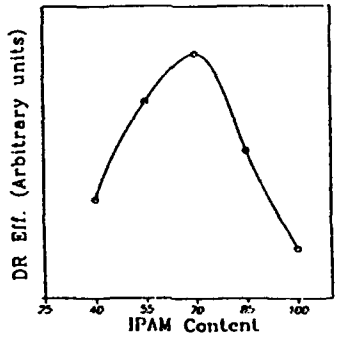

Figure 8b: DR efficiency of IPAM copolymers.

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